THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 2 FEBRUARY, 1934 NUMBER 2

The Infrared Absorption Spectra of Nitrogen Dioxide and Tetroxide*

LOUIS HARRIS AND G. W. KING, *Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology*
(Received December 6, 1933)

The absorption spectra from 1 to 4μ of pure NO_2–N_2O_4 mixtures in a long tube were examined with a rocksalt and a quartz spectrometer. Several new bands were discovered from 1.9 to 4μ in the spectra of both NO_2 and N_2O_4. The NO_2 bands were analyzed as combinations of two fundamentals. The N_2O_4 bands were interpreted as combinations and harmonics of reported fundamentals. Three bands of N_2O_4 lie at shorter wave-lengths than correspond to the work of dissociation into 2 NO_2. A study of the symmetry properties shows that only those models where the NO_2 groups are joined by the nitrogen atoms would give rise to the observed infrared spectrum. Some features of the spectrum seem to be in favor of the existence of molecules where the NO_2 groups do not lie in the same plane.

INTRODUCTION

THE infrared absorption spectrum of the NO_2–N_2O_4 system has recently been investigated by several authors.[1, 2, 3, 4] We present in this paper the absorption spectrum, in the nearer infrared, of deep layers of some very pure NO_2 and N_2O_4,[5] as resolved by a rocksalt and by a quartz prism spectrometer. The spectrum of N_2O_4 in this region is composed of distinct bands which we consider to be combinations of the fundamentals reported by Sutherland.[1, 6] Two bands of NO_2 are discovered which we have interpreted as combinations of some undiscovered fundamental with one already known.

APPARATUS

Since the gases react with cements, metals and greases, they were confined in an all quartz absorption tube 100 cm long and 2.54 cm diameter, surrounded by an electric furnace. The windows were of carefully selected quartz and, although only 2.0 mm thick, were opaque beyond 4μ.

In order to reach this wave-length no other quartz was permitted in the optical path, in one series of experiments. The light of a Nernst glower was reflected by gold mirrors through the tube and then through a minimum deviation 60° rocksalt prism spectrometer. A Coblentz twenty-two junction thermopile traversed the spectrum with twice the angular velocity of the prism and the angle of (minimum) deviation of the incident light was measured by a graduated table reading to five seconds. This spectrometer was calibrated by the simple minimum deviation formula. Paschen's[7] values for the refractive index of rocksalt corrected to 21°C were used but so few points are given in this region of inflection that a considerable uncertainty in the wave-length arises

* Contribution No. 319.

[1] G. B. B. M. Sutherland, Proc. Roy. Soc. **A141**, 342 (1933).

[2] R. Schaffert, J. Chem. Phys. **1**, 507 (1933).

[3] A. B. D. Cassie and R. L. Bailey, Nature **131**, 239 (1933).

[4] J. Strong and T. Woo, Phys. Rev. **42**, 267 (1932).

[5] The preparation will be described elsewhere by L. Harris and W. S. Benedict.

[6] G. B. B. M. Sutherland, Proc. Roy. Soc. **A141**, 535 (1933).

[7] Paschen, Ann. d. Physik [4] **26**, 120, 1029 (1908).

($\pm 0.003\mu$). The prism was kept at constant temperature within 0.1°C since $d\lambda/dt = 0.015\mu$/degree.

In the region of transparency of quartz ($< 2.8\mu$) much higher dispersion was obtained by means of a quartz half-prism constant deviation spectrometer of large aperture. The light of a 1000 watt tungsten lamp was passed through the meter tube by quartz lenses. Monochromatic light from the exit slit was focussed on a Kipp thermopile. A graduated drum measured the angle between the half prisms in radians but the constants of the calibration had to be evaluated by locating mercury emission lines (to 1.71μ). Calibration from the positions of the bands of common substances did not seem advisable as the values in the literature do not agree.

With each instrument the positions of the absorption bands of water-vapor[8] in the air and of three NO_2 and N_2O_4 bands[9] agreed well within the experimental error of 0.012μ with the published values.

The intensity of the transmitted light was measured by the thermopiles and a Leeds and Northrup HS galvanometer, giving reproducible transmission curves within one percent. Two to ten readings were taken per slit width (see figures) and the curves determined several times at each absorption band. The tube was emptied by freezing out the contents into a side arm with "dry ice" (commercial solid CO_2). The transmission of the full tube was found at 21°C and 130°C with the rocksalt instrument and at 24°C and 160°C with the quartz, where the calculated compositions were as follows:[10]

Temperature of absorption tube	(°C)	21	24	120	130	160
Temperature of reservoir	(°C)	21	24	−12	50	75
Partial pressure reduced to 0°C of NO_2 (P_{NO_2}) mm Hg		188	217	188	1034	1184
of N_2O_4 ($P_{N_2O_4}$) mm Hg		511	495	2	86	12

Treatment of Data

Although we are not primarily interested in the magnitudes of the absorption coefficients, it is necessary to resolve the absorption curve for each equilibrium mixture into its two components in order to locate the bands of each constituent. Using logarithms of transmissions, a correction was applied throughout the spectrum to the absorption curves (rocksalt data) of the mixtures by subtracting the absorption due to the minor constituent, calculated by Beer's law from the absorption curve of the other mixture where this species was now in excess. It was assumed that the absorption coefficients do not depend on the temperature or pressure under this resolution; later experiments with NO_2 showed Beer's law was valid within our experimental error, as might be expected from the fact[1] that the fundamentals even under high resolution show no detailed structure.

With the quartz spectrometer, the absorption tube was heated to 160°C, where the gas was practically pure NO_2, so that no correction was applied for the absorption of the small amount of N_2O_4 present. To find the absorption of pure N_2O_4 we had first to estimate the absorption of the NO_2 in the gas mixture at 24°C by another series of measurements made with the tube at 120°C and the reservoir at −12° where the gas was all NO_2, and at the same pressure as in the mixture at 24°C.

Fig. 1 shows the curves for NO_2 at 130°C and N_2O_4 at 21°C as obtained with the rocksalt spectrometer. Fig. 2 gives the absorption of NO_2 at 160°C and N_2O_4 at 24°C under the higher dispersion, all curves having been corrected as outlined above. A comparison shows how the apparent absorption increases with the resolution and how overlapping bands shift the maxima.

Results

The absorption coefficients of NO_2 from 1 to 2.1μ and of N_2O_4 from 0.75 to 1.9μ are less than 0.0003 atm.$^{-1}$cm^{-1} (three percent being the accuracy of measurements of weak absorption), unless there are bands narrower than the slit width (shown in figures). The spectra of both gases between 1.9 and 4μ consist of more or less isolated bands whose maxima are given in Tables I and II.

We use Mecke's notation, which is identified with the notation Sutherland used for the fundamentals in a later table. If the z-axis be taken

[8] G. Hettner, Ann. d. Physik [4] **55**, 476 (1918).

[9] See tables below.

[10] M. Bodenstein, Zeits. f. physik. Chemie **100**, 68 (1922).

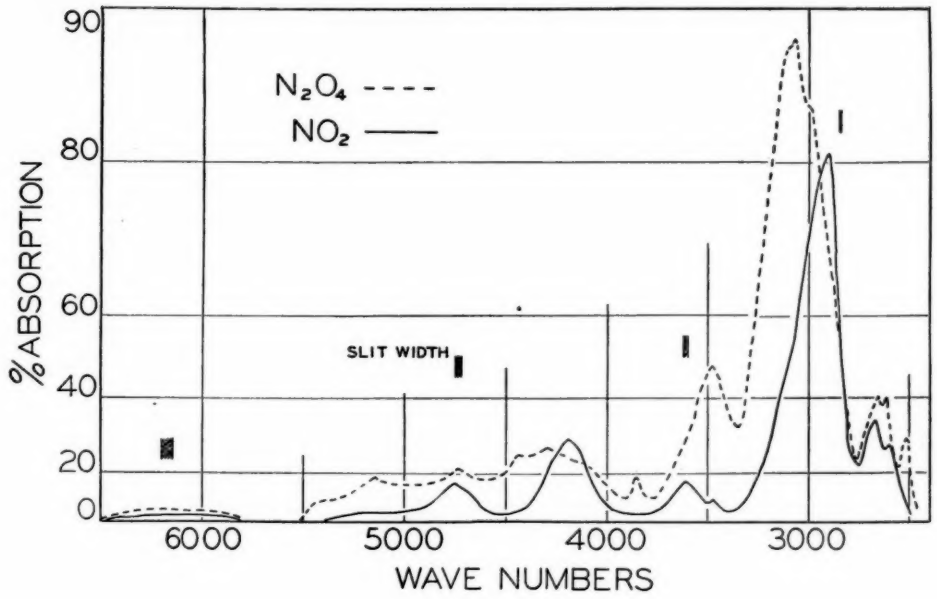

90
80
60
40
20
0
% ABSORPTION
N_2O_4 ----
NO_2 ——
SLIT WIDTH
6000
5000
4000
3000
WAVE NUMBERS

FIG. 1.

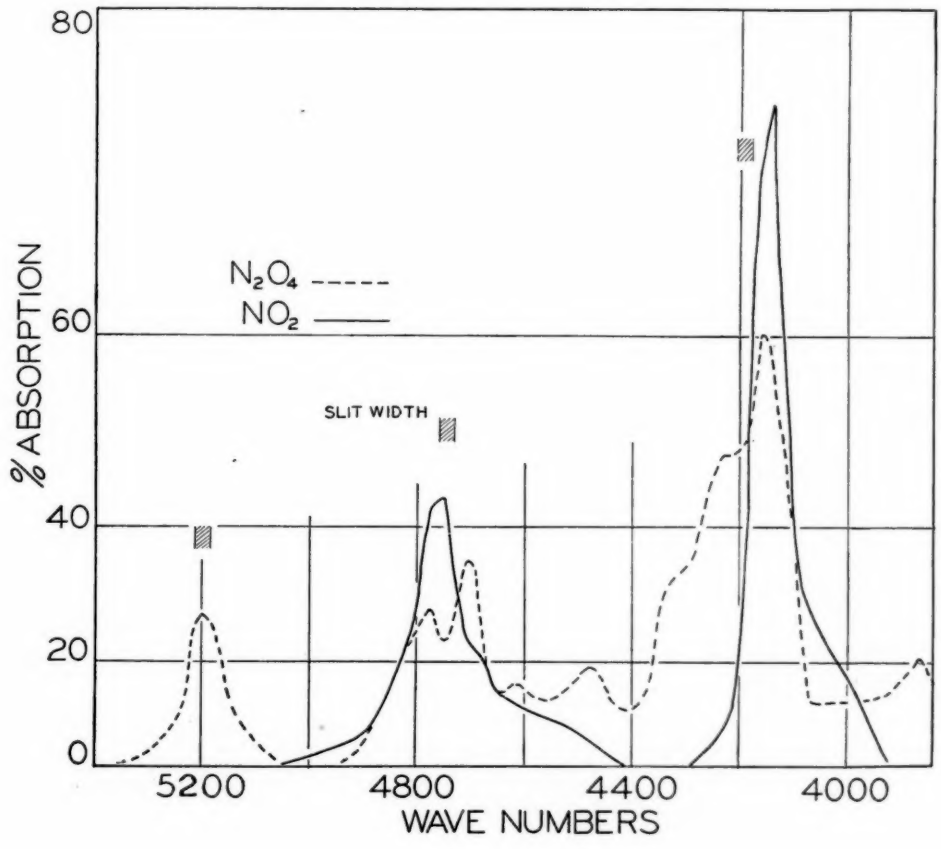

80
60
40
20
0
% ABSORPTION
N_2O_4 -----
NO_2 ——
SLIT WIDTH
5200
4800
4400
4000
WAVE NUMBERS

FIG. 2.

TABLE I. *NO_2 at 130° and 160°C.*

Observed here cm^{-1}	Observed by others cm^{-1}	Calculated cm^{-1}	Analysis	Intensity
	648[1, 2, 3]	—	δ_π	Strong
	(1321)[5]	1321	ν_π	—
	1621[1, 2, 3]	1621	ν_σ	Very strong
	2220[1]	2236	$\nu_\sigma+\delta_\pi$	Medium
2601				
2667	2630[5]	2630	$2\nu_\pi$	Medium
2905	2910[1]	2893	$\nu_\sigma+\nu_\pi$	Very strong
ca. 3200	3242[1]	3206	$2\nu_\sigma$	No maximum but strong absorption
3454				
3597		3540	$\nu_\sigma+\nu_\pi+\delta_\pi$	Weak
ca. 3930		3927	$3\nu_\pi$	Hidden weak maximum
4140		4151	$\nu_\sigma+2\nu_\pi$	Strong
4560		4427	$2\nu_\sigma+\nu_\pi$	Hidden weak maximum
4753		4753	$3\nu_\sigma$	Medium

TABLE II. *N_2O_4 at 21° and 24°C.*

Observed here cm^{-1}	Observed by others cm^{-1}	Calculated cm^{-1}	Analysis	Intensity
	380[4]	—	$\delta_{\sigma a}$	—
	682[1]	—	$\delta_{\sigma' a}$	—
	752[1]	—	$\delta_{\pi a}$	—
	880[4]	880	$\delta_{\sigma a}+\delta_{\sigma s}$	—
	948[1]	965	$\nu_{2\pi s}+\delta_{\sigma' a}$	—
	1265[1]	—	$\nu_{\pi a}$	—
	1744[1]	—	$\nu_{\sigma a}$	—
	1750	1765	$\nu_{\pi a}+\delta_{\sigma s}$	—
		2078	$\nu_{\pi a}+\delta_{\pi s}$	
	2060[1]	2087	$\nu_{\pi s}(2)+\delta_{\pi a}$	—
		2135		
		(2476)	$\nu_{\sigma s}+\delta_{\pi a}$	—
2501		2557	$\nu_{\sigma a}+\delta_{\pi s}$	Medium
2608		2602		Strong
2649	2620[1]	2650	$\nu_{\pi a}+\nu_{\pi s}(2)$	Strong
2967	2975[1]	2989	$\nu_{\sigma s}+\nu_{\pi a}$	
		3009	perp. $\nu_\sigma+\nu_{\pi a}$	Very strong
3077		3081		
3091		3129	$\nu_{\sigma a}+\nu_{\pi s}(2)$	
3478		3468	$\nu_{\sigma a}+\nu_{\sigma s}$	Strong
		3488	perp. $2\nu_\sigma$	
		(3795)	$3\nu_{\pi a}$	
3861		3985*	$2\nu_{\pi s}+\nu_{\pi a}$	Weak
4160		4274*	$\nu_{\sigma a}+2\nu_{\pi a}$	Strong
4230		4349*	$\nu_{\sigma s}+\nu_{\pi a}+\nu_{\pi s}$	Medium
4340		4464*	$\nu_{\sigma a}+2\nu_{\pi s}$	Weak
4478		—	—	Weak
4620		4713*	$2\nu_{\sigma s}+\nu_{\pi a}$	Weak
		4753*	$2\nu_{\sigma a}+\nu_{\pi a}$	
4706		4753*	perp. $2\nu_\sigma+\nu_{\pi a}$	Medium
		4828*	$\nu_{\sigma a}+\nu_{\sigma s}+\nu_{\pi s}$	
4778		4848*	perp. $2\nu_\sigma+\nu_{\pi s}$	Medium
		5192	$2\nu_{\sigma s}+\nu_{\sigma a}$	
5197		5232	$3\nu_{\sigma a}$ or $3\nu_\sigma$	Medium

* Anharmonicity correction (not attempted) would justify this assignment.

through the N−N bond, then π signifies $\parallel$ to z; σ, $\perp$ to z; σ', $\perp$ to z and $\perp$ to the plane of the NO_2 groups; the vibrations of the NO_2 groups will be symmetric (s) or antisymmetric (a) with respect to the center of symmetry. The assignment is for the plane molecule; for the perpendicular model the assignment is the same, except that the (σs) and (σa) vibrations become identical, as will be discussed below.

THE SPECTRUM OF NO_2

Only two fundamentals have been reported for NO_2, at 1621 and 648 cm^{-1}.[1, 2, 3] If the molecule is linear the third frequency ν_π can be calculated to be about 1000 cm^{-1} and although the fundamental would be absent in the infrared, combinations should be expected. The absence of a third frequency however is not a definite indication of a linear molecule; there are several triangular molecules known where the ν_π frequency appears very weakly. Harris and Benedict[5] have found separations in the ultraviolet spectrum of NO_2 of 1321 and 2630 cm^{-1}, which are very reasonable values for ν_π, $2\nu_\pi$ of a triangular molecule. These values fit the infrared data very much better than a calculated 1000 cm^{-1}. If ν_π is weak, the other π overtones, $v_\sigma\nu_\sigma$, $v_\sigma\nu_\sigma+\nu_\pi$, etc., ($v_\sigma$ even) will also be weak (cf. H_2O,[11]). Table I shows that indeed the only strong bands are the σ-bands of odd v_σ, their sharpness warranting the evaluation of three anharmonicity terms. The frequencies were calculated from

$$E=1681(v_\sigma+\tfrac{1}{2})+1357(v_\pi+\tfrac{1}{2})-18(v_\sigma+\tfrac{1}{2})^2 -6(v_\pi+\tfrac{1}{2})^2-48(v_\sigma+\tfrac{1}{2})(v_\pi+\tfrac{1}{2}).$$

The intensity of $\nu_\sigma+\nu_\pi$ and $\nu_\sigma+2\nu_\pi$ is reflected in the magnitude of the interaction constant, -48 cm^{-1}.

Bands reported[1, 2] at 1350–75 cm^{-1} are probably the frequency 1365 cm^{-1} of nitrite ions[1] formed by reaction of the gases with the rocksalt windows, avoided in the present work. These bands may have masked the weak NO_2 fundamental at 1321 cm^{-1}.

THE SPECTRUM OF N_2O_4

The new bands between 1 and 4μ can be satisfactorily interpreted as combinations of the re-

[11] Mecke *et al.*, Zeits. f. Physik **81**, 313 *et seq.* (1933).

TABLE III.

Representation	Operators E	$C_2(z)$	$C_2(y)$	$C_2(x)$	C_i	$C_s(z)$	$C_s(y)$	$C_s(x)$	Configurations
A_{1s}	1	1	1	1	1	1	1	1	*Zero state* $\nu_{\pi s}=\nu_2=13\frac{37}{82}$ $\delta_{\pi s}=\nu_4=813$ $\nu_{2\pi s}=\nu_8=283$
A_{1a}	1	1	1	1	−1	−1	−1	−1	*Free rotation* ν_7
A_{2s}	1	1	−1	−1	1	1	−1	−1	
A_{2a}	1	1	−1	−1	−1	−1	1	1	Z, $\nu_{\pi a}=\nu_1=1265$ $\delta_{\pi a}=\nu_3=752$ $\delta_{\sigma' s}=\nu_{12}$
B_{1s}	1	−1	1	−1	1	−1	1	−1	
B_{1a}	1	−1	1	−1	−1	1	−1	1	Y, $\nu_{\sigma a}=\nu_5=1744$ $\delta_{\sigma a}=\nu_9=380$
B_{2s}	1	−1	−1	1	1	−1	−1	1	$\nu_{\sigma s}=\nu_6=1724$ $\delta_{\sigma s}=\nu_{10}=500$
B_{2a}	1	−1	−1	1	−1	1	1	−1	X, $\delta_{\sigma' a}=\nu_{11}=682$

TABLE IV.

Representation	Operators E	$C_2(z)$	$2C_iC_4,-4(z)$	$2C_2(x,y)$	$2C_s'(x',y')$	Configurations
A_1	1	1	1	1	1	*Zero state* $\nu_{\pi s}=1360$ $\nu_{2\pi s}=283$ $\delta_{\pi s}=813$
A_2	1	1	1	−1	−1	
B_1	1	1	−1	1	−1	*Free rotation*
B_2	1	1	−1	−1	1	Z $\nu_{\pi a}=1260$ $\delta_{\pi a}=752$
E_0	2	−2	0	0	0	X, Y, $\nu_{\sigma}=1744$ $\delta_{\sigma}=500\backsim382$ $\delta_{\sigma'}=\backsim682$

ported infrared and Raman fundamental frequencies. As was the case with the data treated by Sutherland, the comparative scarcity of bands in this region (if combinations and overtones of all twelve fundamentals appeared the absorption at the present dispersion would appear nearly continuous) is positive evidence for a symmetrical N_2O_4 molecule, undoubtedly one where the NO_2 groups are joined by the nitrogen atoms. However, we must examine the data for indications of two well-populated configurations of N_2O_4 of nearly the same energy, in which the NO_2 groups lie in the same plane or are mutually perpendicular, and for indications of free rotation through both these positions upon surmounting a comparatively low hill of potential energy.

Neglecting for the present the interaction with free rotation, the other eleven fundamental frequencies may be arranged among the various representations of the symmetry groups corresponding to the equilibrium positions. The selection rules of combination, derived from symmetry considerations,[12, 13] are equally rigorous for the two configurations and are equally compatible with the observed spectra.

Plane N_2O_4 has the symmetry properties of group V_h which has the irreducible operators and representations given by Table III; the z-axis is chosen as the N−N bond; the y-axis lies perpendicular to this in the plane of the molecule.

The selection rule for the infrared, namely

$$\int (\partial m/\partial q_i)\psi_{\text{init.}}(\xi)\bar{\psi}_{\text{final}}(\xi)d\xi$$

must be positive in all symmetry operations. Applied to this group, it shows that for transitions from the zero state (1) no fundamentals of symmetrical (s) vibrations, or (2) even overtones of any fundamental are active and (3) there are no combinations of s with s or of a with a or (4) of vibrations lying in representations with the first subscript the same. The most intense of the permitted combinations have been given in Table II.

The perpendicular molecule is of the V_d group, described by Table IV.

The outstanding difference between the groups is seen to be the occurrence in V_d of the degenerate representation E_0, wherein the 6 σ-vibrations coalesce to form three (not two as stated by Sutherland) degenerate pairs, which are all active. However, as only the three (σa) are active in V_h, there will be the same number of observable infrared fundamentals as in V_d. That the values of the Raman frequencies[6] do not coincide with those of the infrared for these pairs cannot be taken as evidence against the existence of the perpendicular form in the gas, as the Raman spectrum was obtained only in the solid, which x-ray studies[14] have shown to be composed of predominantly plane molecules. In the overtones and combination bands also, V_d gives the same number of active bands as V_h. In V_d, even-numbered harmonics of the σ-vibrations will occur (with pronounced Q branches) but with less than the full intensity expected of states of increased (degenerate) weight, since the characters of the product, E_0^2, split into the sum $A_1+B_1+B_2$, of which only the last is active, the representation of the Z-moment. All combinations of the σ-vibrations with each other and with other types of vibrations are also permitted.

[12] L. Tisza, Zeits. f. Physik **82**, 48 (1933).

[13] R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

[14] S. B. Hendricks, Zeits. f. Physik **70**, 699 (1931).

Throughout, a correlation of the permitted combinations of V_d with V_h may be made.

In Table II we have shown how the permitted combinations, on either model, account for the main features of the spectrum. The following considerations, however, lead us to suspect that both models participate in giving the observed bands.

The point at issue is whether the σ-vibrations have one frequency or two. Only ν_σ is observed with certainty in overtones and combinations. In the region of 1750 cm^{-1} the envelope of absorption as observed by Sutherland is wide and asymmetrical with a deep minimum which Sutherland interpreted as the central gap to be expected in the fundamental $\nu_{\sigma a}$ where the moment vibrated along the middle axis of inertia of an asymmetrical top and hence as evidence for the plane molecule. A rough calculation with the aid of Dennison's diagrams[15, 16] reveals, however, that for a molecule as heavy as N_2O_4 the central gap would not be so wide as observed and that in all probability the envelope, under the attainable resolution, would appear with a wide and weak central maximum (ratio of moments 1 : 1.8 : 3.1). In the perpendicular model, N_2O_4 is a symmetrical top (ratio 1 : 2.6 : 2.6) and would have a somewhat stronger central maximum. It is therefore probable that the observed absorption is due to the fundamental $\nu_{\sigma(a)} = 1744$ cm^{-1}, on which is superposed the permitted combination $\nu_{\pi a} + \delta_{\sigma(s)} = 1765$ cm^{-1}. The Raman frequency of the solid (plane) occurs at 1724 cm^{-1}; hence we must look for combinations of 1744 and 1724 from the plane and for combinations of 1744 only from the perpendicular molecules; if rotational oscillation is present the bands will lie between these limits. In the region of the fundamental the presence of weak asymmetric absorption lying to shorter frequencies of 1744 may be due to the 1724 ($\nu_{\sigma s}$) coupling with ν_{rot} to become weakly active.

The first "overtone" would lie at 3468 cm^{-1} (less some anharmonicity term which must be present if the band is to appear with appreciable intensity) if plane, and at 3488 cm^{-1} if perpendicular. The observed band at 3478 cm^{-1} is presumably the center of the overlapping of a plane model combination, $\nu_{\sigma a} + \nu_{\sigma s} = 3468$ cm^{-1} with the perpendicular frequency $2\nu_\sigma = 3488$ cm^{-1}.

The calculated separation between $2\nu_{\sigma(a)} + \nu_{\pi a}$ and $\nu_{\sigma(a)} + \nu_{\sigma(s)} + \nu_{\pi s}$ is 75 cm^{-1} for the plane, 95 cm^{-1} for the perpendicular molecule. The observed is 70 ± 5 cm^{-1} but a correction for slit-width would increase this value. Moreover the envelope at 4778 cm^{-1} seems to be composed of the bands of both types of molecules.

All these facts are evidence for the existence of an appreciable fraction of molecules in the gas in which the NO_2 groups do not lie in the same plane. It would be of interest to examine the envelopes of these overtone bands under high resolution in the attempt to decide whether the plane or the perpendicular form is the equilibrium position of the gaseous N_2O_4 molecule and to determine the height of the potential hill hindering free rotation. However, the discussion we have given should make it clear that an unambiguous decision will be attended with difficulties.

As the single N—N bond should have no directional properties and the forces between the rather distant O atoms on opposite NO_2 groups are doubtless small, a considerable fraction of the molecules, even at low temperatures, will probably be oscillating widely about the equilibrium position, if not rotating freely. The oscillation motion will be strongly coupled to the other modes of vibration in such a way that these deviate from the frequencies and selection rules typical of the equilibrium position towards the frequencies and selection rules of the less symmetrical configurations taken up during the oscillation. For completely free rotation, the coupling will be so strong that the other vibrations will resemble exactly neither those of the plane nor the perpendicular models but will be intermediate between them. The long stretches of continuous absorption observed in certain regions may indicate some degree of free rotation.

Dissociation of N_2O_4

The energy of dissociation of N_2O_4 into $2NO_2$ as given by equilibrium constants[10] is 12.6 kcal., equivalent to 4440 cm^{-1}. N_2O_4 absorbs light of shorter wave-length than corresponds to its energy of dissociation in three strong, well-defined isolated bands, centers at 5197, 4778 and 4706 cm^{-1}.

[15] Dennison, Rev. Mod. Phys. **3**, 280 (1931).
[16] Gerhard and Dennison, Phys. Rev. **43**, 197 (1933).

We have analyzed these bands as combinations of vibrations within the NO_2 groups, corresponding to the bands $3\nu_\sigma$ and $2\nu_\sigma+\nu_\pi$ of single NO_2 and not of the vibration of the N—N bond ($\nu_{2\pi_s}$). As a result of this absorption the molecule is elevated to a quantized level of a potential surface above the convergence limit of the decomposition frequency ($\nu_{2\pi_s}$). The molecule may now either redistribute its energy into the N—N bond and decompose by a radiationless transfer through the col above the convergence limit or it may, more probably, lose this energy by collisions. The actual occurrence of discontinuous absorption is of interest from the standpoint of the old "radiation hypothesis" and as a verification of a phenomenon that has long been suspected to be possible.

Even if all the energy absorbed in this region resulted in the decomposition of the molecule, the amount of infrared light needed to oppose measurably the thermal rate of formation is exceedingly high at ordinary temperatures (10^8 mols/sec. requiring 10^9 kcal./sec.). It may however be possible to decompose, at low temperatures, the white vitreous solid N_2O_4 into red NO_2 by infrared radiation between 1.92 and 2.25μ.

Acknowledgments

The authors are deeply indebted to Dr. W. S. Benedict for his continued interest and valuable suggestions during the course of this work. We wish also to thank Professor G. R. Harrison of the Department of Physics for the use of the rocksalt spectrometer and Dr. H. M. O'Bryan for his assistance in the use of this instrument.

Crystal Structures and Expansion Anomalies of MnO, MnS, FeO, Fe_3O_4 Between 100°K and 200°K*

BENNETT S. ELLEFSON† AND NELSON W. TAYLOR,‡ *School of Chemistry, University of Minnesota, Minneapolis, Minnesota*

(Received November 18, 1933)

(1) Determinations have been made of structure type and lattice constants of MnO, MnS, FeO and Fe_3O_4 at temperatures near those at which these substances show specific heat anomalies. (2) No major structure changes were apparent in the x-ray patterns. All structures are cubic at all investigated temperatures. Lattice constant data indicate similarity in the abnormal expansion behavior of MnS and FeO and of MnO and Fe_3O_4. (3) The specific heat and expansion anomalies are probably due to electron transitions within certain atoms in the crystal lattice and may be analogous to the behavior of metallic iron at 765°C, or of quartz at 575°C.

INTRODUCTION

ACCORDING to results of recent experiments carried out by Millar[1] and Anderson[2] at the Pacific Experiment Station of the Bureau of Mines, MnO, FeO, Fe_3O_4 and MnS show anomalies in their specific heat curves. Each curve shows a cusp or hump superimposed upon the normal ascending trend. The plots of heat capacity *versus* temperature for these four compounds are reproduced in Figs. 2, 3, 4 and 5. For exact numerical data reference should be made to the original publication.

Whenever a transition in state occurs, there results an abnormal absorption or evolution of energy. Consequently, the relation between heat capacities and temperature is quite helpful in locating such transitions. The change from one structure to another is usually accompanied by a heat absorption or evolution over a relatively short temperature range.

Experiments have been reported which show that the abnormal absorption of energy is not always accompanied by change in crystal structure. Simon[3] discovered anomalous specific heat behavior in ammonium chloride at some point between 223° and 243°K. Investigation of the crystal structure at these low temperatures by Simon and v. Simson[4, 5] shows anomalous behavior at 242.3°K for ammonium fluoride, at 242.6°K in the case of ammonium chloride, at 235°K in the case of ammonium bromide and at 230.5°K in the case of ammonium iodide.

Klinkhardt[6] in his work on specific heat of iron found two outstanding abnormalities in the specific heat curve. One of these abnormalities, occurring in the neighborhood of 906°C, represents a sharp drop in the specific heat curve and is explained by Westgren and Lind's[7] work showing a change from the body-centered cubic lattice of the alpha iron to the face-centered cubic lattice of the gamma iron. The other specific heat anomaly which takes place over a considerable temperature range and which reaches a maximum at 765°C, cannot be accounted for on the basis of crystal structure change. However, it is interesting to note that the peak of this curve occurs at the same point at which the iron loses its ferromagnetic properties.[8]

* Presented by Nelson W. Taylor before the Division of Physical and Inorganic Chemistry at the Washington meeting of the American Chemical Society, 1933.

† Submitted in partial fulfillment of the requirements for the degree of Master of Science, June 1933.

‡ Present address: Head, Department of Ceramics, The Pennsylvania State College, State College, Pa.

[1] R. Millar, J. Am. Chem. Soc. **50**, 1875–83 (1928); **51**, 215–22 (1929).

[2] C. T. Anderson, J. Am. Chem. Soc. **53**, 476–83 (1931).

[3] F. Simon, Ann. d. Physik **68**, 241 (1922).

[4] F. Simon and v. Simson, Naturwiss. **38**, 880 (1926).

[5] F. Simon and v. Simson, Zeits. f. physik. Chemie **129**, 339 (1927).

[6] H. Klinkhardt, Ann. d. Physik **84**, 167–200 (1927).

[7] A. Westgren and A. Lind, Zeits. f. physik. Chemie **98**, 181 (1921).

[8] Weiss, J. de Physique **7**, 249 (1908).

Apparatus

The source of x-rays for all pictures taken in this experiment is a Siegbahn metal x-ray tube with an iron target.[9] The camera is one designed by Taylor.[10] Slight modifications were made to reduce thermal capacity. The specimen is mounted on a wire passing vertically through the camera at its center. The film is placed in a cylindrical envelope and fastened securely about the outer side. For the purpose of thermal insulation, the camera is packed in cotton in a wooden box lined on the inside with tin foil. There are three small openings in the box, one on the side for the slit system of the camera, one for the thermocouple and ground leads and the final one on top for a gas inlet. The outer end of the slit system is flush with the outside edge of the box to permit as great insulation as possible.

Temperature Measurements

A copper-advance thermocouple was constructed from No. 30 insulated copper wire and No. 30 insulated "advance" wire. Three advance wires and one copper wire lead to the variable junction, the wires at these points being soldered by means of tin solder.

The potentials generated by this thermocouple were measured by means of a Leeds and Northrup Type K Potentiometer No. 169339 with lower-limit voltage readings at 0.000001 volt. The potentiometer was standardized by means of a Weston Standard Cell having a voltage of 1.0188. The same standard cell was used throughout all the experiments.

Calibration of the thermocouple was carried out according to the method described by Adams.[11] This method involves the determination of a correction curve showing deviations of e.m.f. from a set of standard values of e.m.f. as given by a general equation. The deviations are obtained by observing the potential generated when one junction is in ice water (0°C or 273°K) and the other junction is in a definite and accurate temperature bath. The standard values for the low temperature calibration were obtained from Volume 1, page 57 of the *International Critical Tables*. The fixed temperature points used were (1) the boiling point of O_2,

$$t=(-183.00+0.0126(p-760) \\ -0.0000065(p-760)^2)$$

where p is the atmospheric pressure in millimeters and t is temperature in degrees centigrade; (2) the melting point of ethyl acetate (−83.6°C); (3) the melting point of mercury (−38.87°C) and (4) the melting point of carbon tetrachloride (−22.9°C). The thermocouple was checked against a calibrated Bureau of Mines platinum resistance thermometer (Wheatstone Bridge, Leeds and Northrup No. 88131) and satisfactory agreement was obtained. The sensitivity of the apparatus used makes thermocouple readings accurate to ±0.1°C.

General Procedure

The general set-up is shown in Fig. 1. *A* and *B* are two 500 cc wide mouth bottles containing solid KOH for removal of CO_2, C is an 800 cc wide mouth bottle containing anhydrous calcium chloride for removal of H_2O, *D* is a 1/2 liter

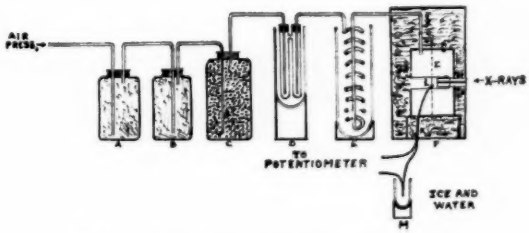


FIG. 1. Low temperature x-ray camera.

Dewar in which is placed a set of 1″×8″ liquid air traps arranged in series, *E* is a 1-liter Dewar containing a meter of 6 mm copper tubing in the shape of a coil, *F* is a wooden box lined with tin foil. Inside this box, packed in cotton, is the camera *G*. *K* represents the thermocouple leads to the variable junction which is fastened to the wire specimen holder *I*, immediately below the point at which the x-rays coming through the slit *H* strike the specimen *L*. *M* is a 250 cc Dewar which contains the ice and water mixture for cold junction. The specimen was ground to powder in

[9] Siegbahn, *Spectroscopy of X-rays*, Oxford University Press (1925).

[10] N. W. Taylor, Rev. Sci. Inst. **2**, 751–55 (1931).

[11] Adams, J. Am. Chem. Soc. **36**, 65 (1914).

an agate mortar and placed on the wire specimen holder by means of collodion. Wood's metal was used in connecting the thermocouple to the specimen holder, since its melting point is so low that it can be applied easily and also will not affect the solder used in making copper-advance connections. A relatively large amount of Wood's metal was used so as to make a thermal reservoir near the specimen.

When the film is in position the only openings remaining in the camera are the tube on the upper side for gas inlet, the slit for x-ray entrance at the side and the tube at the bottom for entrance of thermocouple leads. Constant temperature was obtained by streaming cooled gas through the camera at such a rate as to counteract exactly heat increase from without.

The thermal capacity of the camera is relatively large so that small variations in the rate of flow of the gas will not be noticeable. However, during the period of an exposure, from two to three hours, air pressure and room temperature changes may require that slight adjustments be made in the rate of flow. Temperature deviations from the constant value desired are considered as being confined to a range of $\pm 0.5°C$.

Pictures of each of the compounds were taken at various temperatures throughout the range. Each is listed in a tabulated form below. In general, a picture of each substance was taken (1) at room temperature, (2) at the temperature corresponding to the peak of the anomaly in the specific heat curve and (3) and (4) at temperatures above and below the anomaly.

Materials

In these experiments we are dealing with the same material as used in the specific heat determinations. We are grateful to Dr. Charles G. Maier of the Bureau of Mines Pacific Experiment Station, Berkeley, California who has kindly supplied the compounds used. Complete details as to the preparation of these compounds are given in the reports on specific heat data.

Measurements

The films were developed and measurements were made on negatives. The distances between outside edges of corresponding lines were measured to an accuracy of 0.1 mm. Under the conditions of the experiment it is impossible to give the exact dimensions of the camera. The temperature measurements made are those of the central wire and not of the camera and hence the radius of the camera cannot be assumed. It is, therefore, necessary to use some standard whose lattice constant is known so that the film may be calibrated. In relation to the compounds studied, the standard chosen must not only give lines which do not coincide with those of the compound but must also give enough lines throughout the range of the film so that calibration will be complete. No measurements of lattice constants of elements for low temperatures are recorded in the literature but, assuming that coefficient-of-expansion data are applicable to the side of a unit cell, we can calculate, on the basis of lattice constant at room temperature and coefficient of expansion data at low temperatures, the value of the lattice constant of the standard at the low temperatures.

Mo was chosen as a standard for the compounds MnS, FeO and Fe_3O_4. In the case of MnO, platinum wire was used, since the diffraction lines of MnO and Mo are coincident to the extent that they cannot be distinguished on the film.

The coefficient of linear expansion of Mo wire is given by Schad and Hidnert[12] as

$$L_t = L_0(1 + 5.15t \times 10^{-6} + 0.00570t^2 \times 10^{-6}),$$

t being the temperature in degrees centigrade. This value agrees very well with results presented by Disch.[13]

Coefficient-of-expansion data for platinum wire given by Dorsey were plotted and the average value over the range in question was obtained from the graph.

Approximate values of the angle of reflection, 2θ, and of $\sin^2\theta$, were obtained by assuming 57.85 mm as the effective diameter of the camera. Then by using the calculated lattice constants for various temperatures, the true values of $\sin^2\theta$ for the reflections from the different planes in the standard were calculated from Bragg's equation.

$$n\lambda = 2d \sin\theta,$$

[12] Schad and Hidnert, Phys. Rev. **13**, 148 (1919).
[13] J. Disch, Zeits. f. Phvsik **5**, 173 (1921).

TABLE I. *Data: MnO series:* III. MnO on Pt wire at 115°K. Film 266: Fe rad., 30 k.v. 15 m.a., 2 hr.: Lattice Constant $Pt=3.904$A, $s=0.06$ cm.

Relative intensity	$2d-s$ (cm)	2θ	Observed $\sin^2\theta$	Calculated $\sin^2\theta$ for Pt lines	Corrected $\sin^2\theta$	Indices	$\sin^2\theta$
st.	12.34	122.21	0.7665		0.7674	(400)	(16) (0.04795)
m.	11.92	118.06	.7352	0.7362 (222)			
st.	11.10	109.93	.6704	.6748 (211)			
st.	9.89	97.95	.5691		.5750	(222)	(12) (.04791)
st.	9.32	92.31	.5209		.5275	(311)	(11) (.04795)
m.	8.90	88.15	.4838	.4908 (220)			
v. s.	7.66	75.86	.3779		.3836	(220)	(8) (.04795)
m.	5.94	58.83	.2412	.2454 (200)			
st.	5.20	51.50	.1887		.1918	(200)	(4) (.04795)
v. st.	4.47	44.37	.1419		.1439	(111)	(3) (.04796)

$\sin^2\theta=0.04795\ (h^2+k^2+l^2)\cdots$FeK$\alpha$

$a_{MnO}=(1.934)^2/(4)\ (0.04795)=4.416$A

which, in case of a cubic lattice, may be written

$$\sin^2\theta=(\lambda^2/4a^2)(h^2+k^2+l^2).$$

The difference between the true and the observed values as plotted on a graph showing the relation between observed $\sin^2\theta$ and correction (difference between true and observed $\sin^2\theta$). By making use of these correction curves, the correct values of $\sin^2\theta$ for all lines were obtained. Since the lines of the standard cover the range of the whole film, these correction curves also eliminate errors that may be due to the film itself, such as warping. The results are listed in tables showing the identification of lines with their respective crystal planes. Although lines due to Fe beta-rays were identified, only values resulting from lines due to Fe alpha-rays were used in calculating the lattice constants. The lattice constants are accurate to ±0.002A.

A typical set of data is presented in Table I, but on account of space similar data for the seventeen studied cases will not be given.

The lattice constants of the several substances are summarized in Table II.

The variations of the lattice constants with temperature are clearly anomalous. Note the minimum in the case of MnO and of Fe_3O_4 at 160°K. Refer to Figs. 2, 3, 4, and 5 for a plot of the lattice constant data. It should be stated that no change in crystal structure type appeared in the x-ray patterns. The only changes appear to be the irregularities in the expansion behavior.

TABLE II. *Lattice constants in Angstrom units at low temperatures.*

MnO	°K	Fe_3O_4	°K	MnS	°K	FeO	°K
4.436	299	8.363	299	5.210	299	4.290	299
4.409	160	8.357	160	5.204	160	4.286	200
4.416	115	8.363	114	5.204	143	4.284	186
4.419	104	8.363	104	5.197	138	4.283	160
				5.192	130		

DISCUSSION

Okamura[14] has carried out dilatometric measurements on magnetite. According to the graph given in his report Fe_3O_4 expands with decrease in temperature from 173°K to 73°K. In the same report, it is stated that x-ray pictures by Nishiyana revealed no change in structure. However, no description of the method used and no values for calculation are given. Two other physical phenomena of interest that occur at the transition point are: (1) an abnormally great increase of specific resistance with decrease in temperature and (2) a sudden fall in intensity of magnetization after having gradually increased with decreasing temperature.

Quoting from Okamura's work:

> So far as the relative position of iron atoms in magnetite is concerned, alpha and beta magnetite have no noticeable difference. It is, however, to be noted that it is difficult to find the position of oxygen atoms in the iron lattice by Debye-Scherrer's method of x-ray analysis. . . . Thus the transformation of magnetite alpha⇄beta is probably due to a small displacement of oxygen atoms in the magnetite.

[14] T. Okamura, Science Reports Tohoku Imp. Univ., First series **21**, 2, 231–241 (1932).

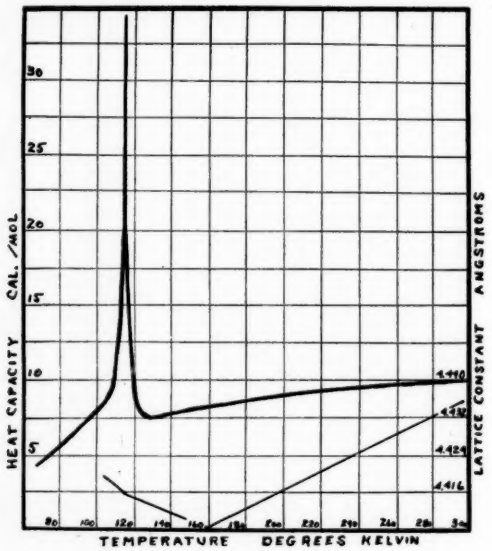


FIG. 2. MnO: Relation between heat capacity, lattice constant and temperature.

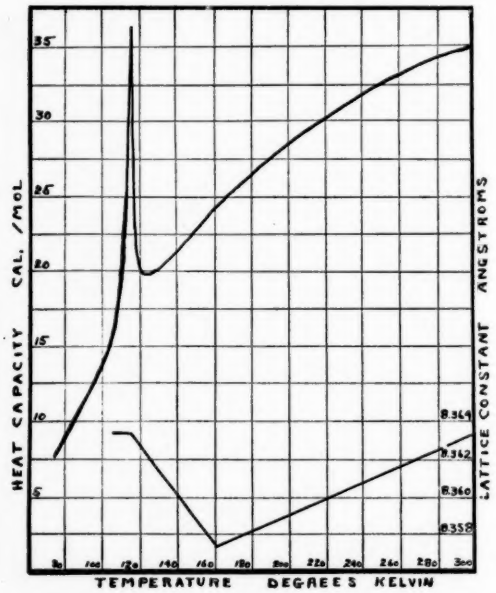


FIG. 3. Fe_3O_4: Relation between heat capacity, lattice constant and temperature.

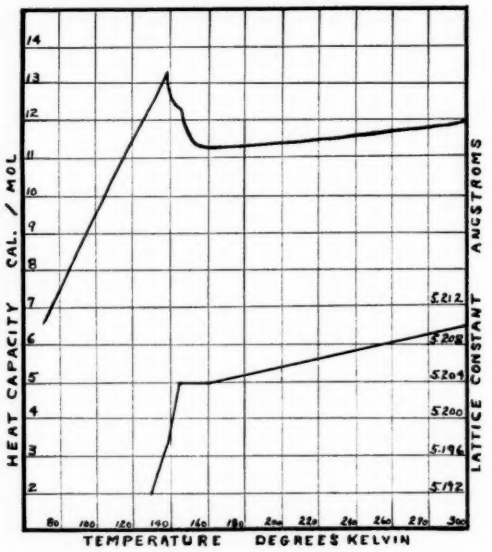


Fig. 4. MnS: Relation between heat capacity, lattice constant and temperature.

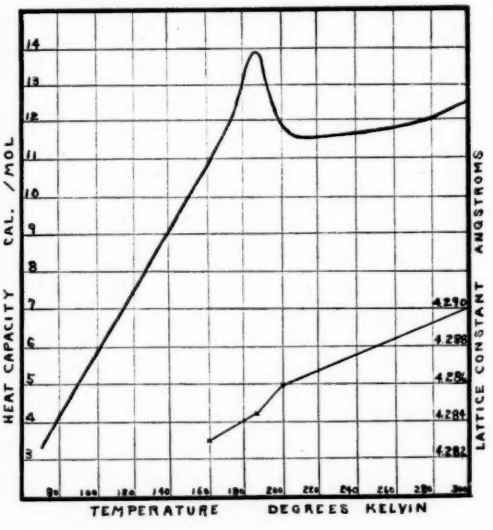


FIG. 5. FeO: Relation between heat capacity, lattice constant and temperature.

Hence, in order to know the nature of this transformation it is necessary to compare the Laue spots of alpha and beta magnetites. So far as any change of physical properties at the transformation temperature is concerned, magnetite shows a similar behavior to that of quartz. That is, quartz (SiO_2) has an allotropic transformation at 573°; this change can be traced by those of thermal expansion, specific heat, electrical conductivity and magnetic susceptibility. Rinne found by means of x-ray analysis that the transformation of quartz alpha$\rightleftarrows$beta is due to a small displacement of oxygen atoms. Thus in all probability the transformation in magnetite is similar to that in quartz. It is very interesting to note that the transformation in magnetite and in quartz which consists only of the small change of distribution of the oxygen atoms in the iron lattice affects the electrical and magnetical properties to a considerable degree. This marked

> effect is probably caused by some change in the valence electron in the atoms, which may reasonably take place as the result of small displacement of atoms in that lattice. Thus the transformation of a substance may consist of three changes, that is,
>
> (1) change of lattice,
> (2) change of state of electrons in atoms,
> (3) change of orientation of atoms.
>
> In the case of magnetite and quartz, change (1) is probably small but (2) and (3) are considerable.

By dilatometric measurements carried out by Simon and Bergmann[15] it is shown that ammonium chloride increases in volume at the transition point, while ammonium bromide and ammonium dihydrogen phosphate gradually contract during the transition interval. Kracek[16] noted an abnormal expansion of sodium nitrate.

Investigations by Southard, Milner and Hendricks[17] on normal amyl ammonium chloride indicate a similar behavior.

On the basis of a wave-mechanical treatment, Pauling[18] shows how many gradual transitions from an oscillatory state to one of rotation can arise in solids where the moments of inertia are small and the intermolecular forces are also small. Such transitions usually are "foreshadowed on the low temperature side by an abnormal increase in heat capacity."

S. B. Hendricks, E. Posnjak and F. C. Kracek have investigated ammonium nitrate[19] and explain some of their results on the basis of rotation of nitrate ions. The abnormalities in ammonium halides to which reference was made at the beginning of this paper are explained on the basis of rotation of ammonium ion.

On the other hand, in solids having strong intermolecular ionic or atomic forces such transitions from oscillation to rotation are less likely. In view of the fact that MnO, FeO, MnS and Fe_3O_4 are all rather polar compounds of high melting point, hardness, etc., they would seem to fall into this latter class. We must therefore look for another interpretation of their anomalous specific heat and expansion behavior.

As far as behavior of the specific heat curve is concerned, Fe at 765°C is quite analogous to the compounds we have studied. Since this abnormality was explained by magnetic changes we may expect them in our compounds. Okamura's work bears out this argument. Of interest in this connection is the fact that CuO shows abnormalities in its specific heat behavior while Cu_2O does not.[1] Cu_2O is diamagnetic whereas CuO is paramagnetic. All of the compounds which we have studied are paramagnetic. J. H. Van Vleck[20] states:

> Even in paramagnetic bodies some anomalies in specific heat curves should be expected. There is a considerable amount of spin coupling between paramagnetic ions due to the Heisenberg exchange effect, provided the material is one of fairly high magnetic concentration, e.g., MnS, MnO, Fe_3O_4. This is presumably the cause of anomalies in MnS and CuO. It might be described as a potentially ferromagnetic body above the Curie point. It should alter the specific heat but it is not at all clear that it should give a cusp in the curve. In fact, the conventional theory gives an anomaly only at the Curie point with no change in specific heat above.

The specific heat curves of MnO and Fe_2O_3 show striking similarity. The abnormality in each case is very great and is confined to about 20° and the peak is at practically the same temperature (115°K for MnO and 114°K for Fe_3O_4). Above the abnormal range and up to 300°K, the C_p curve is a continuation of the initial stage and also is concave to the temperature axis in each case. Curiously enough both substances show contraction as the temperature rises through the abnormal range from 104° to 160°, followed by expansion at higher temperatures. It may be of interest to bear in mind that Fe^{+++} ion in magnetite has essentially the same electron structure as Mn^{++} in MnO. In the case of MnS, the bond is probably not of a simple ionic type because of polarization of the sulfide ion.

The specific heat curves of MnS and FeO are similar to one another in shape but different from MnO and Fe_3O_4. They both have relatively large expansion through the abnormal interval fol-

[15] F. Simon and R. Bergmann, Zeits. f. physik. Chemie **B8**, 255 (1930).

[16] F. C. Kracek, J. Am. Chem. Soc. **53**, 2609–24 (1931).

[17] Southard, Milner and S. B. Hendricks, J. Chem. Phys. **1**, 95–102 (1933).

[18] L. Pauling, Phys. Rev. **36**, 430 (1930).

[19] S. B. Hendricks, E. Posnjak and F. C. Kracek, J. Am. Chem. Soc. **54**, 2766–86 (1932).

[20] J. H. Van Vleck, private communication.

lowed by smaller expansions at higher temperatures.

This is seen from the following data:

Temperature range	160–200°K	200–299°K
Coefficient of expansion of FeO	1.75×10^{-5}	0.94×10^{-5}
Temperature range	130–160°K	160–299°K
Coefficient of expansion of MnS	7.7×10^{-5}	0.83×10^{-5}

It is difficult to say that there is a real difference in the behavior of MnS and FeO as compared with MnO and Fe_3O_4 but the data would seem to indicate it. Magnetic susceptibility measurements over the abnormal temperature range of each of the substances may bring out more clearly any difference.

The Calculation of Thermodynamic Quantities from Spectroscopic Data for Polyatomic Molecules; the Free Energy, Entropy and Heat Capacity of Steam

A. R. GORDON, *Chemistry Department, University of Toronto*

(Received December 11, 1933)

The methods already developed by Gordon and Barnes for computing thermodynamic quantities from the band spectrum of a diatomic molecule are extended to deal with the case of the triatomic unsymmetrical rotator. The free energy, entropy and heat capacity of steam are computed for the temperature range 298.1–1500°K from the spectroscopic data of Mecke and his associates. From the free energy so calculated, the known spectroscopic free energies of carbon monoxide, carbon dioxide and hydrogen, and the thermal data of Rossini, revised values of the equilibrium constant for the water-gas reaction are computed. The numbers so obtained are in close agreement with the experimental results of Neumann and Koehler and of Emmett and Schultz.

THE calculation of thermodynamic quantities from the band spectrum of a diatomic molecule has been discussed in detail by various authors[1] and a number of procedures have been developed which avoid the principal difficulties of summation. The corresponding calculation for the polyatomic case has, in general, received scant attention primarily, no doubt, because the requisite experimental data have been lacking. In a recent series of papers, however, Mecke and his associates[2] have presented a reasonably satisfactory analysis of the rotational-vibrational spectrum of steam and although there are still some uncertainties as to the changes in the spectroscopic constants in the higher vibrational states, it is now possible to obtain reliable values of the free energy, entropy and heat capacity for moderate temperatures at least. Moreover, the series which arise in this case are typical of those which will occur in similar calculations for other triatomic unsymmetrical rotators, e.g., SO_2 and H_2S, and it therefore seems justifiable to consider the case of steam in some detail. Indeed, steam provides a particularly good test for any method of approximation, since its rotational-vibrational interaction terms are exceptionally large.

The approximations discussed here are an extension of those developed by Gordon and Barnes[3] for diatomic molecules and the problem is really one of reducing the "state sum" and its derivatives to such a form that the tabulated diatomic functions can be used in their evaluation.

THE EVALUATION OF THE STATE SUM AND THE CALCULATION OF THE FREE ENERGY

The rotational-vibrational energy levels for a triatomic unsymmetrical rotator will, in general, depend on the three fundamental frequencies of the molecule and on its three principal moments of inertia. The frequencies are distinguished by the subscripts δ, π and σ, the corresponding vibrational quantum numbers being v_δ, v_π and v_σ; in the expression for the energy levels, not only will terms occur involving the first and second powers of the vibrational quantum numbers but also "cross terms" of the type $v_\delta \cdot v_\pi$, etc.; moreover, the moments of inertia[4] A, B and C will themselves be

[1] Mulholland, Proc. Camb. Phil. Soc. **24**, 280 (1928); Sutherland, Proc. Camb. Phil. Soc. **26**, 402 (1930); Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932); Gordon and Barnes, J. Chem. Phys. **1**, 297 (1933); Kassel, Phys. Rev. **43**, 364 (1933); J. Chem. Phys. **1**, 576 (1933).

[2] Mecke, Zeits. f. Physik **81**, 313 (1933); Baumann and Mecke, Zeits. f. Physik **81**, 445 (1933); Freudenberg and Mecke, Zeits. f. Physik **81**, 465 (1933).

[3] Gordon and Barnes, J. Chem. Phys. **1**, 297 (1933).

[4] Throughout this paper it is assumed that $A < B < C$.

functions of v_δ, v_π and v_σ. If the molecule is of the type RXY with non-spinning nuclei, the summation over the rotational levels for a given vibrational state is replaced by its limiting value for high temperatures:

$$Q_R \approx \exp(\sigma_{BC}/4)\cdot q_v\cdot(1+\sigma_{BC}/12-\sigma_B\sigma_C/12\sigma_A), \tag{1}$$

where

$$q_v = 8\pi^2 M_v(2\pi kT/h^2)^{\frac{3}{2}} = (\pi/\sigma_A\sigma_B\sigma_C)^{\frac{1}{2}}; \qquad M_v = (A_vB_vC_v)^{\frac{1}{2}};$$

$$\sigma_A,\ \sigma_B,\ \sigma_C = (h^2/8\pi^2kT)\cdot(1/A_v,\ 1/B_v,\ 1/C_v); \qquad \sigma_{BC} = (\sigma_B\sigma_C)^{\frac{1}{2}}$$

and the subscript v stands for $v_\delta v_\pi v_\sigma$. The error introduced by this approximation is discussed in the note at the end of this paper; it is there shown that the approximation is justifiable in any case likely to occur in practice, provided the temperature is 300°K or more.

If, as in the case of steam, there are two equivalent atoms in the molecule each possessing j_S units of nuclear spin, the rotational state sum becomes

$$Q_R \approx \exp(\sigma_{BC}/4)\cdot q_v\cdot(1+\sigma_{BC}/12-\sigma_B\sigma_C/12\sigma_A)\cdot(2j_S+1)^2/2. \tag{2}$$

The vibrational terms in the expression for the energy levels will be of the type

$$\epsilon_v = (\epsilon_v)_\delta + (\epsilon_v)_\pi + (\epsilon_v)_\sigma + \epsilon_i, \tag{3}$$

where

$$(\epsilon_v)_\delta = (v_\delta+\tfrac{1}{2})\omega_\delta - (v_\delta+\tfrac{1}{2})^2\omega_\delta\chi_\delta, \tag{4}$$

$$\epsilon_i = -y_{\delta\pi}\cdot v_\delta v_\pi - y_{\pi\sigma}\cdot v_\pi v_\sigma - y_{\sigma\delta}\cdot v_\sigma v_\delta \tag{5}$$

with definitions similar to (4) for $(\epsilon_v)_\pi$ and $(\epsilon_v)_\sigma$. Thus the rotational-vibrational state sum, Q_{RV}, may be written

$$Q_{RV} = \Sigma \exp[-\epsilon_v/kT]\cdot\exp(\sigma_{BC}/4)\cdot q_v\times(1+\sigma_{BC}/12-\sigma_B\sigma_C/12\sigma_A)\cdot(2j_S+1)^2/2, \tag{6}$$

where the summation is to run over all values of v_δ, v_π and v_σ.

Since A_v, B_v and C_v can all be expressed in terms of their values in the lowest vibrational state plus certain linear and quadratic terms in the vibrational quantum numbers, it follows that q_v can be replaced by an expression of the type

$$q_v = q_0(1+a_\delta v_\delta + a_\pi v_\pi + a_\sigma v_\sigma + b_\delta v_\delta^2 + \cdots + c_{\delta\pi}\cdot v_\delta v_\pi + \cdots), \tag{7}$$

where q_0 is the value of q_v for $v_\delta = v_\pi = v_\sigma = 0$, the a's, b's and c's are numerical constants and the dots after a plus sign indicate two terms obtained by permuting δ, π and σ in the term immediately preceding it.

Since ϵ_i/kT is in general small, $\exp[\epsilon_i/kT]$ can be expanded in a power series and by an obvious rearrangement the logarithm of the state sum can then be written

$$\ln Q_{RV} + E_0/RT = (\ln Q_V + \epsilon_0/kT)_\delta + (\ln Q_v + \epsilon_0/kT)_\pi + (\ln Q_v + \epsilon_0/kT)_\sigma + \sigma_{BC}/4 + \ln(2j_S+1)^2 q_0/2 + \ln(1+r_i), \tag{8}$$

where

$$r_i = (y_{\delta\pi}/kT)\cdot(\bar{v})_\delta(\bar{v})_\pi + \cdots + \tfrac{1}{2}(y_{\delta\pi}/kT)^2\cdot(\overline{v^2})_\delta\cdot(\overline{v^2})_\pi + \cdots + \tfrac{1}{2}(y_{\delta\pi}/kT)\cdot(y_{\pi\sigma}/kT)\cdot(\bar{v})_\delta(\overline{v^2})_\pi(\bar{v})_\sigma + \cdots + a_\delta(\bar{v})_\delta + \cdots + b_\delta(\overline{v^2})_\delta + \cdots + c_{\delta\pi}(\bar{v})_\delta\cdot(\bar{v}_\pi) + \cdots + \sigma_{BC}/12 - \sigma_B\sigma_C/12\sigma_A, \tag{9}$$

$$(\ln Q_V + \epsilon_0/kT)_\delta = \ln\Sigma\exp[-(v_\delta\omega_\delta - (v_\delta^2+v_\delta)\omega_\delta\chi_\delta)/kT], \tag{10}$$

$$(\bar{v})_\delta = (\Sigma v_\delta\cdot\exp[-(\epsilon_v)_\delta/kT])/(Q_V)_\delta, \tag{11}$$

$$(\overline{v^2})_\delta = (\Sigma v_\delta^2\cdot\exp[-(\epsilon_v)_\delta/kT])/(Q_V)_\delta, \tag{12}$$

with similar definitions for symbols involving π and σ. Since numerical values of $(\ln Q_V+\epsilon_0/kT)$, $\bar{v}$ and $\overline{v^2}$ can be found from Gordon and Barnes'[3] Tables I, II, V and IX or by means of the approximations discussed in their Example 4, for given values of $w=\omega/kT$ and χ, it follows that the numerical value of the expression on the right of Eq. (8) can be found at once. If r_i is small in comparison with unity, Eq. (8) can be still further simplified, giving

$$\ln Q_{RV}+E_0/RT\approx(\ln Q_V+\epsilon_0/kT)_\delta+\cdots+\ln(2j_S+1)^2q_0/2 +(y_{\delta\pi}/kT)\cdot(\bar{v})_\delta\cdot(\bar{v})_\pi+\cdots+a_\delta(\bar{v})_\delta+\cdots+b_\delta(\overline{v^2})_\delta+\sigma_{BC}/3-\sigma_B\sigma_C/12\sigma_A. \quad (13)$$

The Calculation of the Rotational-Vibrational Entropy and Heat Capacity

Since $S_{RV}=R\ln Q_{RV}+RT\partial\ln Q_{RV}/\partial T$ and $C_{RV}=T\partial S_{RV}/\partial T$ it follows from Eq. (8) that

$$S_{RV}/R=(S_V/R)_\delta+(S_V/R_V)_\pi+(S_V/R)_\sigma+\ln(2j_S+1)^2q_0/2+3/2+\ln(1+r_i)+(T\partial r_i/\partial T)/(1+r_i), \quad (14)$$

$$C_{RV}/R=(C_V/R)_\delta+(C_V/R)_\pi+(C_V/R)_\sigma+3/2 +\{T\partial(T\partial r_i/\partial T)/\partial T\}/(1+r_i)+(T\partial r_i/\partial T)/(1+r_i)-(T\partial r_i/\partial T)^2/(1+r_i)^2, \quad (15)$$

where $(S_V)_\delta$ and $(C_V)_\delta$ stand for the entropy and heat capacity of an anharmonic oscillator whose energy levels are given by Eq. (4), with similar definitions for symbols involving π and σ. The expressions for $T\partial r_i/\partial T$ and $T\partial(T\partial r_i/\partial T)/\partial T$ can be readily written down by means of the typical relations,

$$T\partial\bar{v}/\partial T=s_1-\bar{v}, \quad (16)$$

$$T\partial\overline{v^2}/\partial T=s_2-\overline{v^2}, \quad (17)$$

$$T\partial s_1/\partial T=c_1, \quad (18)$$

$$T\partial s_2/\partial T=c_2, \quad (19)$$

$$T\partial(\bar{v})_\delta\cdot(\bar{v})_\pi/\partial T=(s_1)_\delta\cdot(\bar{v})_\pi+(\bar{v})_\delta\cdot(s_1)_\pi-2(\bar{v})_\delta\cdot(\bar{v})_\pi, \quad (20)$$

$$T\partial\{(\bar{v})_\delta\cdot(\bar{v})_\pi/T\}\partial T=\{(s_1)_\delta\cdot(\bar{v})_\pi+(\bar{v})_\delta\cdot(s_1)_\pi-3(\bar{v})_\delta\cdot(\bar{v})_\pi\}/T, \quad (21)$$

$$T\partial(s_1)_\delta\cdot(\bar{v})_\pi/\partial T=(c_1)_\delta\cdot(\bar{v})_\pi+(s_1)_\delta\cdot(s_1)_\pi-(s_1)_\delta\cdot(\bar{v})_\pi, \quad (22)$$

$$T\partial\{(s_1)_\delta\cdot(\bar{v})_\pi/T\}/\partial T=\{(c_1)_\delta(\bar{v})_\pi+(s_1)_\delta\cdot(s_1)_\pi-2(s_1)_\delta\cdot(\bar{v})_\pi\}/T. \quad (23)$$

Since numerical values of S_V/R, C_V/R, s_1, s_2, c_1 and c_2 can be found from Gordon and Barnes' tables for given values of ω/kT and χ, Eqs. (14) and (15) may be used to find an approximate value of the rotational-vibrational entropy and heat capacity. Alternatively and to a somewhat poorer approximation, from Eq. (13)

$$S_{RV}/R=(S_V/R)_\delta+(S_V/R)_\pi+(S_V/R)_\sigma+\ln(2j_S+1)^2q_0/2+3/2 +(y_{\delta\pi}/kT)\cdot\{(s_1)_\delta\cdot(\bar{v})_\pi+(\bar{v})_\delta\cdot(s_1)_\pi-2(\bar{v})_\delta\cdot(\bar{v})_\pi\}+\cdots +a_\delta(s_1)_\delta+a_\pi(s_1)_\pi+a_\sigma(s_1)_\sigma+b_\delta(s_2)_\delta+\cdots \quad (24)$$

$$C_{RV}/R=(C_V/R)_\delta+(C_V/R)_\pi+(C_V/R)_\sigma+3/2 +(y_{\delta\pi}/kT)\cdot\{(c_1)_\delta\cdot(\bar{v})_\pi+(\bar{v})_\delta\cdot(c_1)_\pi+2(s_1)_\delta\cdot(s_1)_\pi-4(s_1)_\delta\cdot(\bar{v})_\pi-4(\bar{v})_\delta\cdot(s_1)_\pi+6(\bar{v})_\delta\cdot(\bar{v})_\pi\} +\cdots+a_\delta(c_1)_\delta+a_\pi(c_1)_\pi+a_\sigma(c_1)_\sigma+b_\delta(c_2)_\delta+\cdots. \quad (25)$$

TABLE I. $T=1500°K$, $hc/k=1.43242$.

	δ	π	σ		δ	π	σ
$w=\omega/kT$	1.5613	3.5715	3.6613	$\bar{v}$	0.287	0.033	0.028
χ	0.01223	0.01872	0.01017	s_1	0.859	0.153	0.134
$\ln Q_V+\epsilon_0/kT$	0.2356	0.0285	0.0260	c_1	1.398	0.446	0.403
	+0.0136	+0.0044	+0.0021				
S_V/R	0.6504	0.1318	0.1226	$\overline{v^2}$	0.46	—	—
	+0.0327	+0.0161	+0.0080				
C_V/R	0.8194	0.3797	0.3629	s_2	1.73	—	—
	+0.0374	+0.0317	+0.0164				
				c_2	4.6	—	—

THE FREE ENERGY, ENTROPY AND HEAT CAPACITY OF STEAM FOR TEMPERATURES UP TO 1500°K

From the data of Freudenberg and Mecke,[2] the vibrational constants in cm^{-1} are: $\omega_\delta=1635$, $\omega_\pi=3740$, $\omega_\sigma=3834$, $\omega_\delta\chi_\delta=20$, $\omega_\pi\chi_\pi=70$, $\omega_\sigma\chi_\sigma=39$, $y_{\delta\pi}=20$, $y_{\pi\sigma}=109$, $y_{\sigma\delta}=20$. The moments of inertia are

$$10^{40}\times A=0.996+0.045v_\sigma+0.026v_\pi-0.098v_\delta,$$
$$10^{40}\times B=1.908+0.014v_\sigma+0.033v_\pi-0.034v_\delta, \quad (26)$$
$$10^{40}\times C=2.981+0.047v_\sigma+0.062v_\pi+0.062v_\delta.$$

While there may be some doubt as to the accuracy of Freudenberg and Mecke's expressions for the moments of inertia in the higher vibrational states, their equations seem reasonably accurate for the states which are of importance in calculations for temperatures below 1500°K. From Eqs. (26)

$$M_v=2.3801\times10^{-60}(1+0.0342v_\sigma+0.0321v_\pi -0.0477v_\delta-0.00147v_\delta^2), \quad (27)$$

the other quadratic terms in the expression for M_v making negligible contributions to the calculated thermodynamic quantities for the temperature range considered.

Table I gives (for $T=1500°K$) the values[5] of ω/kT and χ for the three fundamental frequencies and also the values of the functions necessary for the calculation; these latter were obtained by interpolation in Gordon and Barnes' tables.

For this temperature, $\ln g_0/2=6.19597$, $\sigma_{BC}/3=0.00369$, $\sigma_B\sigma_C/12\sigma_A=0.00039$. Hence, excluding the nuclear spin contributions to the free energy and entropy, the approximate values of $\ln Q_{RV}+E_0/RT$, S_{RV}/R and C_{RV}/R from Eqs. (13), (24) and (25) are 6.4975, 8.6261 and 3.113, respectively; the "exact" values[6] from Eq. (6) are 6.9474, 8.6258 and 3.112.

The contributions of the vibrational interaction terms involving $y_{\delta\pi}$, $y_{\pi\sigma}$ and $y_{\sigma\delta}$ to $\ln Q_{RV}+E_0/RT$ are only 0.00018, 0.00009 and 0.00015 for this temperature; the corresponding items for S_{RV}/R are 0.00102, 0.00071 and 0.00089, while for C_{RV}/R they are 0.0039, 0.0039 and 0.0035, respectively. The y-terms are thus of much less importance than the rotational-vibrational interaction terms, i.e., those involving a_δ, a_π, a_σ and b_δ, which contribute -0.01236, -0.03403 and -0.0453 to $\ln Q_{RV}+E_0/RT$, S_{RV}/R and C_{RV}/R, respectively.

Table II gives the numerical values[5] of $-(F°-E_0°)/T$, $S°$ and $C_P°$ for steam for the temperature range 298.1–1500°K, the rotational-vibrational contributions being computed by means of Eqs. (13), (24) and (25). None of the values of $-(F°-E_0°)/T$ and $S°$ includes the nuclear spin contribution of the two hydrogen atoms, $2R\ln 2=2.754$ cal./deg.; this must be added to the entries if the table is to be used in conjunction with Giauque's table for hydrogen.[7] The third decimal place has been retained in the table merely for convenience in interpolation.

From Table II and the data for hydrogen[7] and

[5] The universal constants used in computing Tables I and II were those given in *International Critical Tables*, Vol. I: $h=6.554\times10^{-27}$, $k=1.372\times10^{-16}$, $C=2.9986\times10^{10}$, $R=1.9869$; hence the additive constant for the translational free energy equation is -7.2671.

[6] These values are exact in the sense that the only error is that introduced by the use of Eq. (1); in the note at the end of this paper it is shown that this error is negligible for 1500°K.

[7] Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

TABLE II. *The free energy, entropy and heat capacity of steam.*

$T°K$	$-(F°-E_0°)/T$	$S°$	$C°_P$	$T°K$	$-(F°-E_0°)/T$	$S°$	$C°_P$
298.1	37.179	45.101	8.000	850	45.627	53.987	9.347
300	37.230	45.151	8.002	900	46.106	54.525	9.497
350	38.452	46.389	8.066	950	46.563	55.043	9.648
400	39.513	47.472	8.155	1000	46.999	55.542	9.799
450	40.452	48.439	8.260	1050	47.418	56.023	9.948
500	41.296	49.315	8.379	1100	47.820	56.489	10.095
550	42.062	50.119	8.504	1150	48.206	56.941	10.240
600	42.765	50.864	8.635	1200	48.579	57.380	10.382
650	43.415	51.561	8.771	1250	48.940	57.807	10.522
700	44.020	52.216	8.910	1300	49.289	58.223	10.656
750	44.587	52.836	9.053	1400	49.956	59.022	10.914
800	45.121	53.425	9.199	1500	50.586	59.783	11.153

oxygen,[8] $\Delta S°_{298.1}$ for the reaction $H_2+O_2/2=H_2O(g)$ is -10.64 cal./deg.; from this in combination with Rossini's accurate value[9] of $\Delta H_{298.1}$, *viz.*, $-57{,}809$ cal., $\Delta F°_{298.1}$ for steam is $-54{,}637$ cal. For liquid water, $S°_{298.1}$ is 16.75 cal./deg. and $\Delta F°_{298.1}$ is $-56{,}690$ cal.

The data of Table II can also be combined with the spectroscopic free energy data for hydrogen,[7] carbon monoxide[10] and carbon dioxide[11] and the thermal data of Rossini[9, 12] to compute the equilibrium constant for the water-gas reaction $CO+H_2O=CO_2+H_2$. $\Delta S°_{298.1}$ is here -10.09, $\Delta H_{298.1}$ is -9814; hence $\Delta F°_{298.1}$ is -6806 cal. and $\Delta E_0°$ is -9646 cal. Table III gives the resulting values of $R\ln K=R\ln(p_{CO}\cdot p_{H_2O}/p_{CO_2}\cdot p_{H_2})$ for the range 600–1500°. The numbers in Table III are on the average about 0.07 cal./deg. less than those previously computed[11] and for the range 900–1259° agree even more closely with the results of Neumann and Koehler's experiments;[13] for example, Neumann and Koehler found $K=1.61$ for 1259°K, while from Table III, $R\ln K$ for this temperature is 0.93, i.e., $K=1.60$. Their results for 15 temperatures in this range show a mean deviation from the numbers obtained by interpolation in Table III of less than $+0.02$ cal./deg. in $R\ln K$; for the range 700°–900°, however, the mean deviation is somewhat larger—about $+0.14$ in $R\ln K$. The indirect measurements of this equilibrium by Emmett and Schultz[14] also agrees satisfactorily with Table III; with three exceptions (773°, 823°, 923°) their results for 8 temperatures between 723° and 1073° agree with the data of the table within ± 0.04 cal./deg. in $R\ln K$.

TABLE III. *The equilibrium constant for the water-gas reaction.*

$T°K$	600	700	800	900	1000
$R\ln K$	−6.57	−4.40	−2.81	−1.62	−0.69
$T°K$	1100	1200	1300	1400	1500
$R\ln K$	+0.04	+0.63	+1.12	+1.53	+1.88

EVALUATION OF THE ROTATIONAL STATE SUM FOR A RIGID UNSYMMETRICAL ROTATOR

The procedure that has been adopted almost universally in the past when it has been necessary to evaluate the rotational state sum for a rotator with three different moments of inertia has been to replace the sum by its limiting value for high temperatures

$$Q_R \approx (\pi/\sigma_A\sigma_B\sigma_C)^{\frac{1}{2}}, \qquad (28)$$

where σ_A, σ_B and σ_C are as defined under Eq. (1) and suitable symmetry and nuclear spin factors are to be applied when necessary. While Eq. (28) is a valid approximation at very high temperatures, there is no general rule for estimating its error in any actual case. In the special case that two of the three moments of inertia are

[8] Johnston and Walker, J. Am. Chem. Soc. **55**, 172 (1933).

[9] Rossini, Bur. Standards J. Research **6**, 1 (1931).

[10] Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).

[11] Gordon, J. Chem. Phys. **1**, 308 (1933).

[12] Rossini, Bur. Standards J. Research **6**, 37 (1931).

[13] Neumann and Koehler, Zeits. f. Elektrochemie **34**, 218 (1928).

[14] Emmett and Schultz, J. Am. Chem. Soc. **51**, 3249 (1929); **52**, 892 (1930); **55**, 1376 (1933).

equal, Viney[15] and Kassel[1] have deduced a relation which serves to evaluate Q_R to a higher degree of accuracy than the uncorrected Eq. (28). If the moments of inertia are A, C and C, their equation may be written, to a first order of approximation

$$Q_R = \exp(\sigma_C/4)\cdot(\pi/\sigma_A\sigma^2{}_C)^{\frac{1}{2}} \cdot\{1+\sigma_C/12-\sigma^2{}_C/12\sigma_A+\cdots\}. \quad (29)$$

In the general case, however, where $A \neq B \neq C$, their method cannot be applied, since the energy is not an explicit function of the moments of inertia. It is apparent, however, that the expression on the right of (29) for a rotator with moments of inertia A, $(BC)^{\frac{1}{2}}$ and $(BC)^{\frac{1}{2}}$, should be a better approximation to the value of the actual rotational state sum than the uncorrected expression on the right of (28). On this plausible assumption the rotational state sum is replaced by the expression on the right of Eq. (1).

To obtain an estimate of the error actually introduced by the use of Eq. (1), the energy levels were calculated for the special case $A=1\times10^{-40}$, $B=2\times10^{-40}$, $C=3\times10^{-40}$, and the state sum and its derivatives were computed. These constants are roughly those for steam and, since they correspond to a molecule as unsymmetrical and with as small moments of inertia as is likely to be met with in practice, they provide a particularly good test of Eq. (1).

The algebraic equations from whose roots the eigenvalues for the rotator can be obtained, have been tabulated by Dennison[16] and by Nielsen,[17] For values of J, the rotational quantum number, $\leqslant 8$, the energy levels were found by solving their equations (see Table IV); for $J \geqslant 9$, the asymptotic formulae of Kramers and Ittman[18] were used. While the latter are not particularly accurate as far as the calculation of individual levels is concerned, it was found by actual computation for $J=7$ and $J=8$ that they give the contributions to Q_R and its derivatives with an accuracy of about 1/5 of a percent. Since even for $T=330°$K (the highest temperature for which the calculation was made), the levels with $J>8$ contribute less than 3 percent of Q_R, 10 percent of Q_R' (see Eq. (33)) and 22 percent of Q_R'' (Eq. (34)), the error introduced by using the asymptotic formulae is, at most, a unit or two in the fourth decimal place of $\ln Q_R$ and S_R/R and in the third decimal place of C_R/R. For lower temperatures for which the relative contribution of the high J states is less, the uncertainty will be still smaller.

For a rigid rotator with three different moments of inertia, there are $2J+1$ distinct levels,[16] each $(2J+1)$-fold degenerate, for each value of the rotational quantum number J; these $2J+1$ levels are distinguished by a quantity τ which takes the $2J+1$ values $-J$, $J+1$, $\cdots$ $J-1$, J, the lowest level (for the given J) being assigned $\tau=-J$ the next lowest $\tau=-J+1$ and so on. The rotational state sum thus becomes

$$Q_R=\sum_{J=0}^{\infty}\sum_{\tau=-J}^{+J}(2J+1)\cdot e^{-\epsilon_{J\tau}/kT} \quad (30)$$

and the rotational entropy and heat capacity are given by

TABLE IV. *Values of* $(8\pi^2\epsilon_{J\tau}/h^2)\times10^{-40}$.
$A=1\times10^{-40}$, $B=2\times10^{-40}$, $C=3\times10^{-40}$.

$J=0$:	0.
$J=1$:	5/6, 4/3, 3/2.
$J=2$:	2.24267, 2.83333, 3.33333, 4.83333, 5.09067.
$J=3$:	4.83333, 5.06325, 6.05848, 7.33333, 7.50000, 10.27008, 10.27485.
$J=4$:	7.88133, 8.00491, 9.63908, 10.63900, 11.09047, 13.66176, 13.69425, 17.69433, 17.69487.
$J=5$:	11.5824, 11.6417, 14.0188, 14.7278, 15.6406, 17.9080, 18.0308, 21.9389, 21.9436, 27.1170, 27.1172.
$J=6$:	15.934, 15.961, 19.126, 19.574, 21.118, 22.999, 23.333, 27.053, 27.075, 32.207, 32.207, 38.540, 38.540.
$J=7$:	20.945, 20.955, 24.900, 25.153, 27.460, 28.916, 29.635, 33.041, 33.122, 38.166, 38.170, 44.473, 44.473, 51.962, 51.962.
$J=8$:	26.616, 26.620, 31.310, 31.441, 34.603, 35.634, 36.930, 39.899, 40.120, 45.003, 45.020, 51.276, 51.276, 58.743, 58.743, 67.385, 67.385.

[15] Viney, Proc. Camb. Phil. Soc. **29**, 142 (1933).

[16] Dennison, Rev. Mod. Phys. **3**, 280 (1931). There are two misprints in Dennison's cubic for $J=7$; he gives

$$x^3-56\alpha x^2+(784\alpha^2+776\beta)x-2304\alpha^3-10584\alpha\beta=0. \quad (A)$$

By a change of variable, Nielsen's[17] corresponding cubic can be written in Dennison's notation

$$x^3-56\alpha x^2+(784\alpha^2+784\beta)x-2304\alpha^3-11584\alpha\beta=0. \quad (B)$$

Eq. (B) fulfills the condition that the energy levels should be the same whether α and β are replaced by $\alpha_1\beta_1$, $\alpha_2\beta_2$ or $\alpha_3\beta_3$.

[17] Nielsen, Phys. Rev. **38**, 1432 (1931).

[18] Kramers and Ittman, Zeits. f. Physik **58**, 217 (1929).

$$S_R/R = Q_R'/Q_R + \ln Q_R, \tag{31}$$

$$C_R/R = Q_R''/Q_R - (Q_R'/Q_R)^2, \tag{32}$$

$$Q_R' = \Sigma\Sigma(2J+1)\cdot(\epsilon_{J\tau}/kT)\cdot\exp\left[-\epsilon_{J\tau}/kT\right], \tag{33}$$

$$Q_R'' = \Sigma\Sigma(2J+1)\cdot(\epsilon_{J\tau}/kT)^2\cdot\exp\left[-\epsilon_{J\tau}/kT\right]. \tag{34}$$

Table IV gives the numerical values of Q_R, Q'_R and Q_R'' as computed from Eqs. (30), (33) and (34) together with the resulting $\ln Q_R + E_0/RT$, S_R/R and C_R/R for $T = 330.44°$, 198.26°, 132.17° and 99.13°K, i.e., for $10^{40}\cdot h^2/8\pi^2 kT = 0.12$, 0.2, 0.3 and 0.4; the table also gives the values obtained by using the approximate expression (1) instead of the exact expressions (30), (33) and (34). It should be noted that if the uncorrected Eq. (28) had been used in place of Eq. (30), the resulting value of $\ln Q_R$ would have been 4.6486 for 330.46° and 2.8427 for 99.13°. It is evident from the table that with the assumed moments of inertia and for room temperature and up, the use of Eq. (1) will not introduce an error of more than 0.001 cal./deg. in $F°/T$ or $S°$, or of more than 0.002 cal./deg. in $C_P°$. Since the case chosen for illustration is a particularly unfavorable one, it seems safe to conclude that Eq. (1) may be used with confidence in similar calculations for other unsymmetrical rotators. For low temperatures, however, the calculated thermodynamic quantities deviate widely from those predicted by Eq. (1); for example, curve *a* of Fig. 1 shows the low temperature rotational heat capacity curve for the rotator of Table IV.

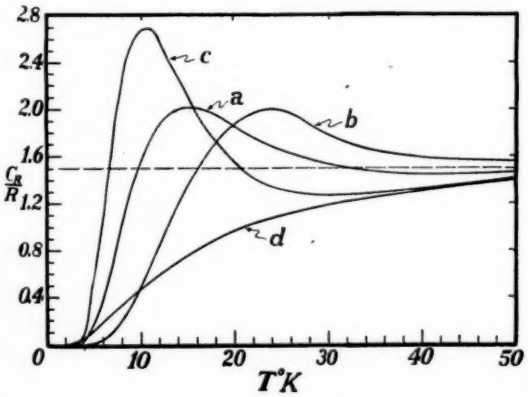


FIG. 1. C_R/R as a function of temperature for an unsymmetrical rotator $A = 1\times10^{-40}$, $B = 2\times10^{-40}$, $C = 3\times10^{-40}$.

In the previous discussion, all questions of symmetry and of nuclear spin have been ignored. If the rotator possesses two equivalent atoms with non-spinning nuclei and if, as in the case of steam, the symmetry axis of the molecule coincides with the intermediate moment of inertia, Dennison[16] has shown that the rotational levels for a given J are alternately symmetric and antisymmetric in the rotational part of the wave function; for $J = 0, 2, 4, \cdots$, the lowest level is symmetric and for $J = 1, 3, \cdots$, antisymmetric, i.e., for either odd or even J, the levels with $\tau = 0, \pm2, \pm4, \cdots$ are symmetric and those $\tau = \pm1, \pm3, \cdots$, antisymmetric. In carrying out the summations of Eqs. (30), (33) and (34) only those rotational levels are to be counted which are of the required symmetry character and, for any temperature so high that the summations over the symmetric and antisymmetric states are the same, this is obviously equivalent to adding the usual Ehrenfest "symmetry term" $-R\ln 2$ to $-F°/T$ and to $S°$ and leaving $C_P°$ unaltered. For the rotator of Table IV at the highest temperature of Table V, this condition is fulfilled, e.g., the sums over the symmetric and antisymmetric levels in Q_R are 52.963 and 52.957, respectively, but for low temperatures this is not the case. For example, if the electronic and vibrational parts of the wave function are such that only symmetric rotational states are to be counted, C_R/R for 198.26°, 132.17° and 99.13° is 1.508, 1.516 and 1.513, respectively; for still lower temperatures, the C_R/R-temperature curve for such a symmetrical molecule is shown in curve *b* of Fig. 1.

If the equivalent atoms, as in steam, each possess one-half unit of nuclear spin (the ex-

TABLE V. $A = 1\times10^{-40}$, $B = 2\times10^{-40}$, $C = 3\times10^{-40}$.

T°K	330.44	198.26	132.17	99.13
Q_R, Eq. (30)	105.92	49.700	27.4189	18.0677
Q_R', Eq. (33)	157.34	73.290	39.9757	26.0384
Q_R'', Eq. (34)	392.76	182.894	99.6460	64.7483
$\ln Q_R + E_0/RT$ Eq. (30)	4.6627	3.9060	3.3112	2.8941
$\ln Q_R + E_0/RT$, Eq. (1)	4.6633	3.9068	3.3109	2.8916
S_R/R, Eq. (30), (33)	6.1482	5.3807	4.7692	4.3353
S_R/R, Eq. (1)	6.1486	5.3824	4.7742	4.3427
C_R/R, Eq. (30), (33), (34)	1.501	1.505	1.509	1.507
C_R/R, Eq. (1)	1.500	1.500	1.500	1.500

tension to other j_S values is obvious) and if the symmetry requirement of the molecule as a whole is such that states symmetric in the rotation are to be combined with states antisymmetric in the spin and *vice versa*, the weight factors will be $2J+1$ for the "para" levels, i.e., those with $\tau=0, \pm2, \cdots$, and $3(2J+1)$ for the "ortho" levels, those with $\tau=\pm1, \pm3, \cdots$. For high temperatures this is equivalent to multiplying Q_R, Q_R' and Q_R'', computed in the absence of symmetry and spin, by $(1/2+3/2)$, that is, to adding the usual symmetry and spin terms $-R\ln 2+2R\ln 2$ to $-F^\circ/T$ and S_0, cf. Eq. (2). This method of allowing for symmetry and spin is thus justified for the rotator of Table IV at the highest temperature of Table V but is not valid for any temperature so low that the high temperature 3 : 1 ratio of ortho to para molecules does not hold (see Table VI

TABLE VI. *Percentage para molecules in the equilibrium mixture.*

T°K	330.44	132.17	66.09	39.65	26.44
Percent	25.00	25.12	25.51	26.52	30.04
T°K	15.86	11.33	7.93	5.66	4.96
Percent	45.58	65.82	87.42	97.41	98.86

which gives the equilibrium percentage of para molecules at various temperatures for the rotator of Table IV). The rotational heat capacity curve of such an equilibrium mixture is shown in c of Fig. 1; for higher temperatures, C_R/R approaches the limiting value 3/2 as in the case of curves a and b; for example, $C_R/R=1.503$, 1.505, 1.503 and 1.501 for 99.13°, 132.17°, 198.26° and 330.44°, respectively.

Since the ortho and para states are non-combining, it is probable that a mixture cooled from high temperatures would retain at low temperature the 3 : 1 ortho-para ratio in a state of "frozen" equilibrium. The rotational heat capacity curve for such a metastable mixture is shown in curve d of Fig. 1; for $T>50$°K in the case chosen for illustration, curves c and d become practically identical.

The possibility of a frozen equilibrium of this kind is of interest in connection with the "Third Law" entropy of steam, which is nearly 0.9 cal./deg. less than the spectroscopic value. If ice consists of such a 3 : 1 mixture and it is assumed that the rotational states of steam carry over into the crystal, the ortho molecules will be trapped at low temperatures in the lowest state antisymmetric in the rotation i.e., $J=1$, $\tau=-1$; this state has a multiplicity of 9 (3 from rotation and 3 from spin) and as a consequence the "zero-point" entropy over and above the high temperature spin entropy $2R\ln 2$ will be $3R/4\cdot\ln 3=1.64$ cal./deg. just as in the case of hydrogen. Giauque and Ashley[19] have pointed out, however, that at temperatures as low as 10°K the only rotations possible in ice are about the symmetry axis of the molecule. Under these conditions the wave functions and eigenvalues are no longer those for a spacial rotator with three moments of inertia, but correspond more nearly to those for a plane (two-dimensional) rotator.[20] The lowest antisymmetric rotational state has $J=1$ and is doubly, not triply, degenerate in the rotation, corresponding to their value $3R/4\cdot\ln 2=1.03$ cal./deg. for the zero-point entropy which is to be added to the third law value.

[19] Giauque and Ashley, Phys. Rev. **43**, 81 (1933).
[20] Pauling, Phys. Rev. **36**, 430 (1930).

Internal Equilibria and Partial Vapor Pressures of Mixtures of Primary Normal Alcohols with Normal Paraffin Hydrocarbons

GUENTHER VON ELBE, *Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh*

(Received November 17, 1933)

1. Heats of mixing for mixtures of primary *n*-alcohols and *n*-hydrocarbons have been determined down to practically infinite alcohol dilution over a temperature range from 10°C to 45°C. It has been found that (1) the heat of mixing is always negative and that the heat absorption, per mol of alcohol, increases with increasing dilution of the alcohols to a limit of 5800 cal. per mol; that the curves of the molar heat absorption against molar alcohol concentration are identical for all investigated systems—the first four primary *n*-alcohols in *n*-hexane and *n*-heptane. Furthermore, reports in the literature that *n*-hydrocarbons may be mixed with each other without any heat effect were confirmed.

2. The present experiments and evidence gathered from the literature indicate that (1) primary *n*-alcohols, in the pure liquid state, are completely associated to double molecules and that when mixed with a hydrocarbon they dissociate into single molecules; (2) that the association takes place between the two hydroxyl groups of two single molecules on account of their electrostatic dipole forces; (3) that the observed heat absorption is entirely due to the dissociation of double molecules, i.e., breaking up of the (electrostatic) hydroxyl bond and that there is no thermal effect of the aliphatic groups in the alcohol molecules upon the hydrocarbon solvent; and (4) that the equilibria between single and double molecules are identical at equal molar concentrations for all primary *n*-alcohols in all *n*-hydrocarbons.

3. This theory leads to an equation for the partial vapor pressures of *n*-alcohols in *n*-hydrocarbons:

$$\log p = \log f - (\lambda - Q)/RT + B - b,$$

where p = the partial vapor pressure at the mol fraction f, λ = the heat of vaporization of pure alcohol, Q = heat of mixing at mol fraction f and temperature T, and b = a universal function of Q. B is determined by the ordinary (simplified) vapor pressure equation

$$\log P = -\lambda/RT + B$$

and is constant over the whole temperature range investigated. λ and B depend upon the nature of the alcohol, while Q and b depend upon molar concentration and temperature.

4. It is shown that after b has been determined once as a function of Q in a specific case, one can calculate partial vapor pressure curves of other systems.

5. An equation has been developed which permits the calculation of the degree of dissociation and therefore Q, for any temperature and concentration.

WHILE extensive experimental material is available on the physical properties of liquid mixtures, it usually appears impossible to obtain an accurate idea of the changes which the components undergo during the process of mixing. Attempts to introduce chemical conceptions, such as the formation of double, triple, etc., molecules, have frequently been made in the past but usually have met with failure; on the other hand, no other general method of treatment has been offered thus far. However, consideration of the experimental data presented in this paper on mixtures of primary normal alcohols with normal paraffin hydrocarbons appears to justify the adoption of a specific and simple picture in this particular case. It may be assumed that similar simple conditions may be found in other systems and further, that the simplicity of the present case may allow an approach to the fundamental laws governing equilibria in liquid systems.

Primary normal alcohols, in the liquid state, show x-ray diagrams which indicate the existence of cybotactic groups containing two sets of planes:[1] one set of planes is produced by the arrangement of the molecules as double molecules, two OH groups being together and the two molecules forming a straight chain, the other by the arrangement of two such double molecules lying side by side with the two pairs of OH groups not directly adjacent but slipped by one another so that the set of planes containing them is not normal to the length of the chain. In Fig. 1, the

[1] Stewart, Chem. Rev. **6**, 483 (1929). Compare also further references there.

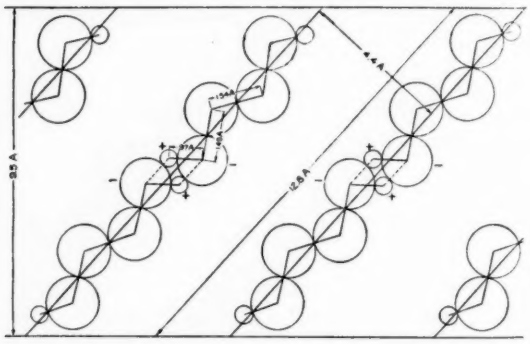


FIG. 1. Cybotactic group of *n*-propyl alcohol.

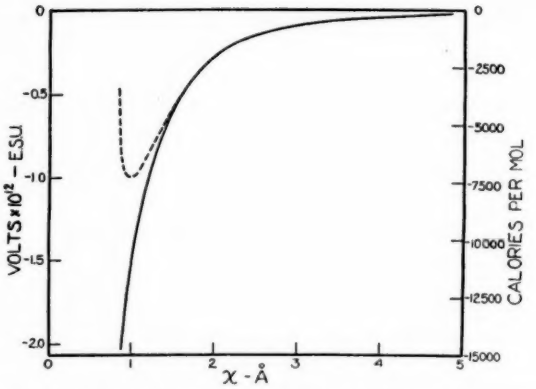


FIG. 2. Estimated curve of the potential energy between two hydroxyl groups.

cybotactic group of *n*-propyl alcohol is shown, from Stewart's data on the distance of the planes. The value of 12.8A for the length of the double molecule is estimated from his formula for the length of *n*-paraffin molecules and additional information on the dimensions of the OH group.[2] The distance between the two adjacent OH groups is assumed arbitrarily to be that of the closest possible approach.

The head-to-head association is certainly caused by the strong electrostatic forces arising from the polar OH groups. The dipole moment of the OH group itself amounts to about 1.6 $\times 10^{-18}$ e.s.u.,[3] which is rather large compared to other groups. On the other hand, the separation of the poles must be rather small, since the distance of the nuclei of the atoms amounts to only 0.97A.[2] It follows that the poles themselves are extraordinarily strong and that two molecules are linked together with considerable force. Information on the strength of this electrostatic bond may be obtained from a paper by M. Dunkel,[4] who shows that the increase of the heat of evaporation of an alcohol over that of the corresponding paraffin is fairly constant throughout the homologous series and amounts, on the average, to 7250 cal. per mol. Since there is no association of alcohol molecules in the gas phase, this value may be interpreted to represent the heat of formation of double molecules. The large value of 7250 cal. per mol—comparable to a chemical bond—suggests that association in the liquid state is practically complete.

[2] Hengstenberg and Mark, Naturwiss. **20**, 539 (1932).
[3] Eucken and Meyer, Phys. Zeits. **30**, 397 (1929).
[4] M. Dunkel, Zeits. f. physik. Chemie **138**, 42 (1928).

Coulomb's law for the potential energy of two dipoles, placed parallel with opposite poles adjacent, is

$$V = -2e^2(1/x - 1/(x^2+y^2)^{\frac{1}{2}}),$$

where e is the pole strength, y the diameter of the polar group and x the interpolar distance. If one identifies y with 0.97A, which is probably too large a value, one may calculate e from the above dipole moment and, correspondingly, the potential energy as a function of x, as shown in Fig. 2. At very close approach, repelling forces will appear. If one places the minimum of potential energy at $X = 1$A and $-V = 7250$ cal. per mol, the dotted curve may represent approximately the combined influence of attraction and repulsion.

Normal hydrocarbons tend to arrange themselves parallel to each other at a distance of 4.6A. There is practically no heat effect if one mixes two different *n*-hydrocarbons with each other, and the partial vapor pressures (p) above the mixture follow Raoult's law:

$$p = fP, \qquad (1)$$

where f = the mol fraction and P the vapor pressure of the pure substance. As shown by thermodynamics, Raoult's law can hold only in the absence of any heat of mixing.

Dunkel[4] has shown that chemical groups, like $-CH_2$, $-CH_3$, preserve their contributions to the intra-molecular force in equal strength in different compounds. The aliphatic radical of an alcohol molecule, therefore, has the same effect upon a

neighboring molecule as if it were a part of a hydrocarbon molecule instead. Therefore, it contributes nothing to the heat of mixing of *n*-alcohols and *n*-hydrocarbons, which appears to be entirely due to the dissociation of the hydroxyl groups.

In view of the above considerations certain predictions can be made about the effects to be observed in the mixing process. At very low alcohol concentrations, the hydroxyl dissociation should be complete. Hence, if association of all alcohols in the pure state is complete, the heat absorbed during mixing should approach a final value identical for all *n*-alcohols in all *n*-hydrocarbons. The present experiments show this to be the case and the value found is 5800 cal. per mol, which is lower than the value of 7250 cal. quoted above because of the higher dielectric constant of the liquid medium. At higher concentrations, equilibria between double and single molecules are established. The degree of dissociation determines the molar heat effect. For equal molar concentrations, this should also be identical for all *n*-alcohols in all *n*-hydrocarbons, since the concentrations of OH groups are identical and the hydrocarbon groups do not influence each other.

Experimental Procedure and Results

The hydrocarbons used were Eastman "practical" hexane and heptane. They were redistilled, especially to insure complete elimination of moisture. The *n*-alcohols used were anhydrous methyl-, ethyl-, *n*-propyl- and *n*-butyl alcohol.

The liquids were mixed in a Dewar flask, constantly stirred, and temperature readings were taken with a Beckmann thermometer. The alcohol sample was contained in a special pipette which was completely immersed in a weighed amount of liquid hydrocarbon and which could be opened from the outside. Figs. 3a and 3b show two different constructions of such pipettes. In Fig. 3a, the alcohol sample is enclosed by mercury and may be pushed out by turning the threaded shaft with the piston on the end. In the construction shown in Fig. 3b, two valves, one on the top, the other on the bottom, may be opened simultaneously, thus releasing the enclosed liquid. The amount of alcohol was determined by weighing the pipettes before and after filling. The

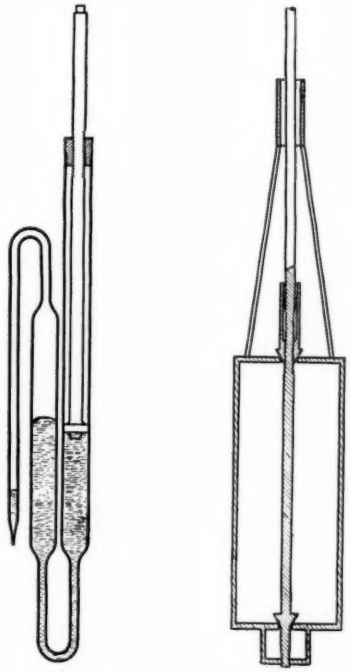


Fig. 3. Sample containers (pipettes) for measuring heats of mixing.

measurements were made by determining the temperature drift before and after mixing. Care was taken to eliminate heat effects due to evaporation by keeping the gas space above the liquid sufficiently small. The heat capacity of vessel and liquid was determined by passing a known current through an immersed resistance wire and determining the temperature change and heating time.

In Fig. 4, the molar heats of mixing the above-named alcohols in heptane and hexane at 29°C are plotted against the concentration (mol per cc). The results of experiments with all the materials fall on one curve, as expected, and approach at infinite dilution a value of $Q_\infty = 5800$ cal. This holds for other temperatures as well, the only difference being a change in the slope of the curves, corresponding to more dissociation at higher temperature and *vice versa*, for any given concentration.

The Dissociation Equilibrium in the Liquid Phase

The equilibrium between double and single molecules, at any temperature T and mol frac-

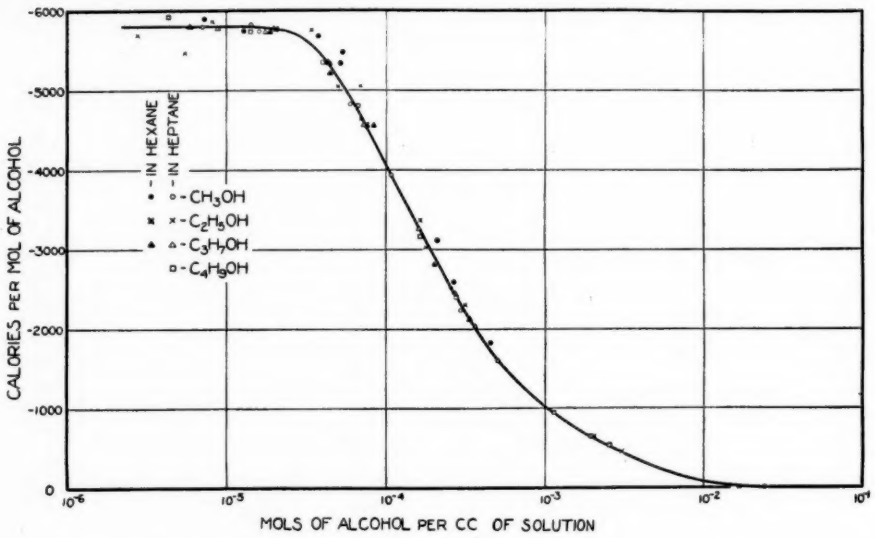


FIG. 4. Heats of mixing of primary normal alcohols in hexane and heptane.

tion f, can be measured by the heat of mixing. The degree of dissociation may be given by

$$\alpha = Q/Q_\infty, \qquad Q_\infty = 5800 \text{ cal.} \tag{2}$$

if the assumption is made that no heat is required to separate double molecules one from another. Since a double molecule resembles a normal hydrocarbon and these show no evidence of a heat of mixing, this assumption is probably justified.

The results of investigations on the dielectric properties of mixtures of alcohols and hydrocarbons[5] may be interpreted from the viewpoint developed thus far. The molar polarization P of a substance in which the molecules are free to assume a perfectly random orientation is represented by the Debye equation, written in the following form:

$$P = \frac{E-1}{E+2}\frac{M}{d} = \frac{4\pi}{3}N + \frac{4\pi N}{9k}\frac{\mu^2}{T}. \tag{3}$$

Furthermore,

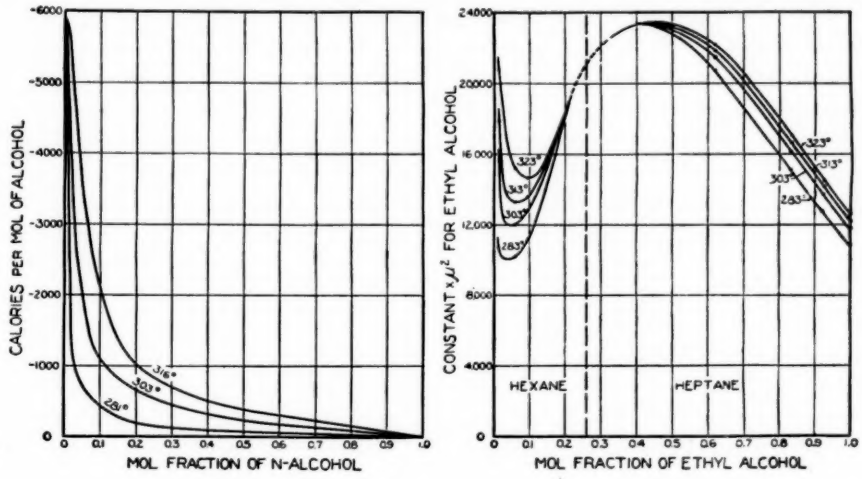
$$[(n^2-1)/(n^2+2)](M/d) = (4\pi/3)N, \tag{4}$$

where n = the index of refraction for light of infinite wave-length, E = the dielectric constant, M = the molecular weight, d = the density, N = Avogadro's number and μ = the dipole moment. The index of refraction should remain about the same for dissociated and undissociated alcohol, as the electronic structure does not change (no "sharing" of electrons). One may, therefore, calculate the factor $(4\pi/9k)N\mu^2$ in (3) from Smyth and Stoops' data. Values thus obtained for ethyl alcohol in hexane at high dilutions and ethyl alcohol in heptane at higher concentrations are plotted as isotherms against the mol fraction f in Fig. 5b. In Fig. 5a, corresponding heats of mixing curves are shown. Both types of curves, from zero concentration upward, drop rapidly in the first part. The reason is the same in both cases: the degree of dissociation rapidly diminishes. A single alcohol molecule possesses a strong dipole moment, while double molecules are only slightly polar, because of their symmetry. The subsequent slope of the curves in Fig. 5b has been discussed by Malsch.[6] It may be pointed out that alcohol double molecules may be deformed by transverse vibrations which bulge the central OH groups out and cause slight polarity. The effect upon an electric field will be increased at higher concentrations when several double molecules are coupled together in the same cybotactic group.

In order to investigate the quantitative connection between degree of dissociation, concen-

[5] Smyth and Stoops, J. Am. Chem. Soc. **51**, 3312 (1929).

[6] Malsch, Phys. Zeits. **33**, 383 (1932).



(a) (b)

FIG. 5. (a) Heats of mixing; (b) Polarization.[5]

tration and temperature, the application of the law of mass action may be attempted:

$$(\alpha^2/(1-\alpha))c = \text{const.} = K, \qquad (5)$$

where c = number of mols per cc. As is shown by Table I, the mass law itself does not hold for any isotherm. Surprisingly, however, van't Hoff's equation

$$\ln K_1/K_2 = (2Q_\infty/R)((T_2-T_1)/T_2T_1) \qquad (6)$$

holds between the K values for equal α's at different temperatures and concentrations, where $2Q_\infty = 11{,}600$ cal. represents the heat of formation of one mol of double molecules from 2 mols of single molecules. This fact permits the calculation of values of the heat of mixing for any temperature and concentration from one experimental isotherm of the heat of mixing.

Since the mass law as expressed by Eq. (5) does not hold, one may adjust it empirically by adding an "activity coefficient." Introducing the factor $(1.492)^{(1-\alpha)/\alpha}/(1.084)^{2\alpha/(1-\alpha)}$ in (5), one obtains

$$\frac{\alpha^2}{1-\alpha} c \times \frac{(1.492)^{(1-\alpha)/\alpha}}{(1.084)^{2\alpha/(1-\alpha)}} = \text{const.} = K^*, \qquad (7)$$

and

$$\ln K_1^*/K_2^* = \ln K_1/K_2 = (2Q_\infty/R)(T_2-T_1)/T_1T_2. \qquad (8)$$

TABLE I. *Application of van't Hoff's equation to the temperature dependency of the dissociation equilibrium.*

T°C	30	44.4	30	44.4	30	42.4	30	42.4
mol per cc $\times 10^4$	.68	1.7	1.0	2.5	2.0	5.1	5.0	10.7
α	.863	.863	.755	.755	.517	.517	.293	.293
$\alpha^2c/(1-\alpha)\times 10^5 = K$	36.8	91	22.8	57.5	11.0	23	6.0	12.9
$\left(\ln \frac{K_1}{K_2}\right)\frac{T_1T_2}{T_1-T_2}R$	11700		12200		11300		11800	
	Mean value = 11750 cal.							
T°C	9.1	30	8.3	42.4	9.2	42.3		
mol per cc $\times 10^4$	.212	1.01	.578	5.6	2.0	13.5		
α	.733	.733	.495	.495	.245	.245		
$\alpha^2c/(1-\alpha)\times 10^5 = K$	4.24	20.3	2.81	27.1	1.59	10.75		
$\left(\ln \frac{K_1}{K_2}\right)\frac{T_1T_2}{T_1-T_2}R$	12300		11900		10400			
	Mean value = 11500 cal.							

TABLE II. *Comparison between mass action law Eq. (5) and new Eq. (7).*

α	0.863	0.755	0.517	0.293
$K\times 10^5$	36.8	22.8	11.0	6.0
$K^*\times 10^5$	14.1	15.8	13.5	14.8

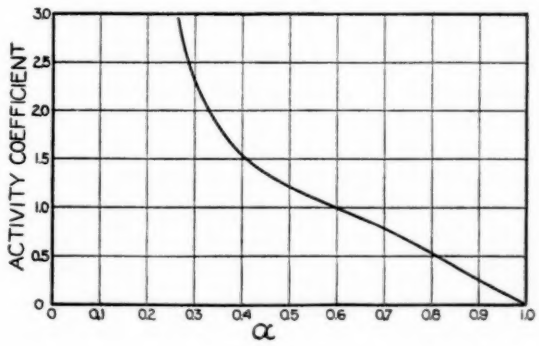


FIG. 6.

In Table II, the K values of Table I, for 30°C, are compared with K^* values. The comparison extends over a wide range of dissociation and shows that Eq. (7) holds satisfactorily. The constancy of K^* obtained here holds for other isotherms as well, of course, because of Eq. (8). In Fig. 6 the activity coefficient is plotted against α. For $\alpha=1$ it becomes zero, for $\alpha=0$ it becomes infinitely large.

Theoretical Discussion

A general theory on equilibria in liquid phases does not exist, except for ionic solutions. The use of the simple mass action law has frequently met with failure in the past and it is not applicable in the present case, even if more than one equilibrium is assumed. In order to account for any of the measured isotherms by assuming triple-, quadruple-, etc., molecules it would be necessary to consider a very large number of such additional equilibria and it would be impossible to account for the simple relationship (8) between the isotherms themselves.

Furthermore, it appears doubtful whether a successful theory may be built upon the assumption of electrostatic forces between the solute molecules, as in the case of ionic solutions. In the first place, deviations from the mass action law are observed even at high dilution, while, on the other hand, the electrostatic dipole potential rapidly diminishes with increasing distance. Second, one will probably find it difficult to fulfill the relationship (8).

Eq. (7) may be formally derived if one is allowed to assume that the osmotic pressures of double and single molecules in separate solutions are proportional to their concentrations and that, if both kinds of molecules are in the same solution together, their respective osmotic pressures are increased for an amount proportional to the concentration of the other component. Thus, if a_1 and a_2 are proportionality factors and c_1 and c_2 the concentrations of single and double molecules, respectively, the increase in the osmotic pressure of the single molecules due to the presence of double molecules amounts to a_1c_2 and the corresponding increase for the double molecules, as compared with their osmotic pressure in a solution which is free of single molecules, amounts to a_2c_1.

With these assumptions, one may now calculate the free energy of transforming 2 mols of single molecules into 1 mol of double molecules. Consider three solutions: one containing single molecules at the standard concentration C_{1s}, another containing double molecules at the standard concentration C_{2s}, and the third containing single and double molecules together at equilibrium concentrations c_1 and c_2. By means of semi-permeable pistons we first compress 2 mols of single molecules from C_{1s} to c_1; second, transfer them into the equilibrium solution; third, remove 1 mol of double molecules from the equilibrium solution and fourth, expand the latter from equilibrium concentration c_2 to standard concentration C_{2s}. In steps one and four the free energy change equals simply $2\,RT \ln C_{1s}/c_1$ and $RT \ln c_2/C_{2s}$, respectively. In steps two and three, work is done because of the increased osmotic pressure of each participant. The work which is done in step two equals $2\,a_1v_1c_2$, where v_1 is the volume which contains one mol of single molecules. Correspondingly in step three, the work done equals $-a_2v_2c_1$, where v_2 is the volume containing one mol of double molecules. The free energy of transforming two mols of single into one mol of double molecules is, therefore, given by

$$\Delta F = 2RT \ln C_{1s}/c_1 - 2a_1v_1c_2 - RT \ln C_{2s}/c_2 + a_2v_2c_1.$$

Introducing $v_1=1/c_1$ and $v_2=1/c_2$ and transposing,

$$\Delta F = RT \ln C_{1s}^2/C_{2s} - RT \ln c_1^2/c_1 - 2(c_2/c_1)a_1 + (c_1/c_2)a_2. \quad (9)$$

Since ΔF, at the temperature T_1, must be independent of any specific equilibrium concentrations c_1 and c_2, one obtains, for constant temperature

$$\ln c_1^2/c_2 + (2c_2/c_1)(a_1/RT) - (c_1/c_2)(a_2/RT) = \text{const.} \quad (10)$$

Introducing the degree of dissociation, α, by means of

$$\alpha = c_1/c \quad (11)$$

and

$$1-\alpha = 2c_2/c, \quad (12)$$

where c is the number of mols $C_nH_{2n-1}OH$ per unit volume, one obtains

$$\ln (2\alpha^2/(1-\alpha))c+((1-\alpha)/\alpha)(a_1/RT) -(2\alpha/(1-\alpha))(a_2/RT)=\text{const.} \quad (13)$$

Since the energy of a fully excited degree of freedom increases in proportion to the temperature and a_1 and a_2 possess the dimensions of an energy, it is plausible to assume that for different temperatures the quotient a_1/RT and a_2/RT remains constant:

$$a_1/RT=\text{const.}=\ln A_1, \quad \text{and} \quad a_2/RT =\text{const.}=\ln A_2. \quad (14)$$

Hence

$$\frac{\alpha^2}{1-\alpha}c\times\frac{A_1^{(1-\alpha)/\alpha}}{A_2^{2\alpha/(1-\alpha)}}=\text{const.}=K^*. \quad (15)$$

Introduction of the numerical value 1.492 for A_1 and 1.084 for A_2 leads to Eq. (7) which is in numerical agreement with the experimental data.

From Eq. (14) one obtains

$$a_1/T=0.7 \text{ cal./deg. per mol and } a_2/T =0.184 \text{ cal./deg. per mol.}$$

These values may possess a physical meaning in connection with the above assumptions. The writer believes, however, that further discussion of these assumptions would be premature.

Partial Vapor Pressures

A knowledge of the heat of mixing makes it possible to deduce an equation for the partial vapor pressures of n-alcohols in the n-hydrocarbons. For this purpose the validity of Raoult's law may be assumed in a modified form:

$$p=f\times P', \quad (16)$$

where P' is a hypothetical vapor pressure which would be established if pure alcohol were in the same state of dissociation as it is in the solution, at the concentration (mol fraction) f. The energy difference between dissociated and undissociated alcohol may be denoted by $\bar{L}_1$; and one may write[7]

$$Q=-\bar{L}_1-(n_{\text{hydr.}}/n_{\text{alc.}})\bar{L}_2. \quad (17)$$

[7] Compare Lewis-Randall, *Thermodynamics*, p. 90 (1923).

The second term represents the change in the heat content of the hydrocarbon solvent. The hydroxyl group of every dissociated alcohol molecule induces a momentum in neighboring hydrocarbon molecules, with the effect that the heat content of the solvent increases in proportion to the alcohol dissociation, while that of the alcohol solute decreases. Substituting, therefore,

$$-\bar{L}_1=\alpha q_1 \quad \text{and} \quad -(n_{\text{hydr.}}/n_{\text{alc.}})\bar{L}_2=-\alpha q_2,$$

one obtains

$$-\bar{L}_1=\alpha q_1=Q+\alpha q_2. \quad (18)$$

Since the specific heats of dissociated and undissociated alcohol are different because of the creation of new degrees of freedom in the dissociated state, there is an entropy difference ΔS. The free energy of changing the alcohol modification characterized by the vapor pressure P' to the normal state characterized by the vapor pressure P is equal to

$$F=RT\ln\frac{P'}{P}=\bar{L}_1-T\Delta S=Q-(T\Delta S-\alpha q_2). \quad (19)$$

It seems again plausible, from the physical picture developed above, that ΔS is determined by the degree of dissociation, i.e., Q, alone, and that both ΔS and q_2 are independent of the nature of either the primary n-alcohol or the paraffin hydrocarbon. Combining (19) and (16) and transposing

$$\ln p=\ln f+\ln P+Q/RT -(1/R)(\Delta S-\alpha q_2/T). \quad (20)$$

For the present limited temperature range, ΔS and q_2/T are fairly constant with temperature. Introducing, therefore,

$$(1/R)(\Delta S-\alpha q_2/T)=b, \quad (21)$$

the term b appears to be essentially a function of Q.

The vapor pressure P is given by the simplified vapor pressure equation, which is very satisfactory over a limited temperature range (*ca.* 100°),

$$\ln P=-\lambda/RT+B, \quad (22)$$

where the constant B may be determined from

the boiling point, and data for λ, in the present case, may be found in the literature.

Combining (20), (21) and (22) one obtains finally

$$\ln p = \ln f - (\lambda - Q)/RT + B - b, \qquad (23)$$

where λ and B depend upon the nature of the alcohol while Q and b depend essentially upon the degree of dissociation, i.e., concentration and temperature.

Measurements are available of the partial vapor pressure curves of methyl alcohol in hexane at 45°C and of ethyl alcohol in heptane at 30°C.[8] Knowing the values of Q and the corresponding values of λ and B for both systems, one may determine b as a function of Q independently for both systems. Fig. 7, which is plotted from the

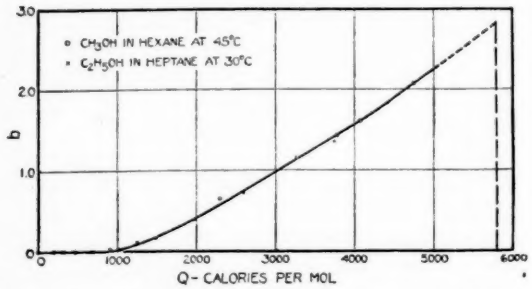


FIG. 7. Identity of Q, b curves (Eq. (20)) for two different alcohol-hydrocarbon systems.

numerical data given in Table III, shows that these functions are indeed identical, as anticipated.

This means, of course, that having once determined $b = f(Q)$ for one system, Eq. (23) will allow one to calculate the partial vapor pressure also for other systems of this type. This generalization seems to be justified despite the fact that the comparison is limited to only two cases because of scarcity of experimental data. It may be pointed out that the two systems under consideration consist of different alcohols in different hydrocarbons at different temperatures and, therefore, provide a very severe test.

Fig. 7 shows that ΔS is not linear in Q, i.e., α. This seems to indicate that the specific heat of the solute alcohol does not increase in proportion to the dissociation. No suggestion can be made,

[8] Ferguson, J. Phys. Chem. **36**, 1123 (1932); Ferguson, Freed and Morris, J. Phys. Chem. **37**, 87 (1933).

TABLE III. *Application of Eq. (23) to mixtures of ethyl alcohol-heptane at 30°C and methyl alcohol-hexane at 45°C.*

		λ	B for $\log_{10} p$ in mm Hg			
Methyl Alcohol		9180	8.83			
Ethyl Alcohol		10000	9.16			
Ethyl Alcohol-Heptane, $t = 30$°C						
f	0.009	0.020	0.038	0.059	0.100	0.200
p (mm Hg)	17.5*	40	50	55	59.5	63.7
Q	5030	3750	2640	1970	1300	770
b	2.28	1.35	0.73	0.39	0.11	0.00
Methyl Alcohol-Hexane, $t = 45$°C						
f	0.030	0.045	0.053	0.070	0.114	0.300
p (mm Hg)	150	229	260	282	300	312
Q	4750	4080	3780	3280	2270	729
b	2.09	1.62	1.43	1.17	0.66	0.00

* Approximate.

at present, to account for this except, perhaps that it may be connected with the peculiar activity coefficient in Eq. (7).

Eq. (23), however, not only allows one to calculate partial vapor pressure curves from calorimetrically measured heats of mixing but to predict, from the slope of these curves, whether the components are miscible in all proportions or separate into two liquid phases. This is demonstrated in Fig. 8. If supersaturation would prevent the separation into two phases, the partial vapor pressure, in the range of supersaturation, would go through a maximum and a minimum. Methyl alcohol and hexane, below 45°C, are no longer miscible in all proportions. The partial vapor pressure curve of methyl alcohol calculated

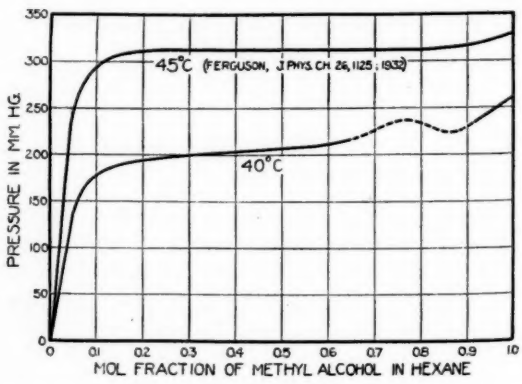


FIG. 8. Formation of two liquid phases in the system methyl alcohol-hexane, indicated by calculated vapor pressure curve.

from (23) for 40°C indeed goes through a maximum and minimum, as shown by the dotted part. The actual extension of the range of immiscibility differs somewhat from the range over which the dotted part in Fig. 8 extends. These limits are very sensitive to the Q values used and the lack of coincidence of the theoretical and experimental range may be accounted for by changes in Q within the limit of error in the heats of mixing data.

The partial vapor pressure curve of the hydrocarbon may, in principle, be determined from the alcohol curve by means of the Duhem-Margules equation

$$-(1-f)d \ln p_{\text{hydr.}}/df = f d \ln p_{\text{alcohol}}/df, \quad (24)$$

which, by combining with Eq. (23), becomes

$$-(1-f)\frac{d \ln p_{\text{hydr.}}}{df} = 1+f\left(\frac{1}{RT}\frac{dQ}{df}-\frac{db}{df}\right). \quad (25)$$

A Summary of the Entropies of Aqueous Ions

WENDELL M. LATIMER, PHILIP W. SCHUTZ AND J. F. G. HICKS, JR., *Chemical Laboratory, University of California*

(Received November 17, 1933)

A critical survey has been made of existing data on the heats, free energies and entropies of reactions involving aqueous ions. These data lead to remarkably consistent values for the ionic entropies. The entropies of 20 positive ions and 12 negative ions have been tabulated.

LATIMER and Buffington[1] in 1926 published a list of ionic entropies which included many of the positive ions and a few of the more common negative ions. These values were based on rather meager data and consequently an accuracy of only two units could be claimed even in the cases where the data were most complete. Since the appearance of this initial article, an intensive program has been in progress in this laboratory with the primary object of establishing these values more definitely. It is felt that the work has progressed to such an extent as to warrant a review of the ionic entropy values now available.

In the initial paper many of the values were based on entropies for the solid salts which had been calculated by the approximate equation given by Latimer[2] or obtained by comparison with similar salts. This uncertainty has since been largely eliminated as a result of the specific heat measurements made in this laboratory.[3] Errors in the heats of solution and activities of salt solutions are still large in certain cases, but recent work by many investigators has reduced these uncertainties also.

The standard state, as in all previous work, of the ionic entropies is the hypothetical one molal solution, that is, a one molal solution of the ion obeying the perfect solution laws and the ions possessing the same partial molal heat content that they have at infinite dilution. $S°_{298.1}$ of H^+ is taken to be zero. The ionic entropies are of course partial molal quantities.

The calculations and the data used have been summarized in Tables I and II.

We have given in Table III the values for the entropies of the aqueous ions which appear to be the most probable. In general we have not taken the simple average of the various determinations summarized in Table I but have given weight to the data which appear to be the most reliable. In addition, we have included the value for fluoride given by Latimer and Buffington,[1] although the complete lack of data on the activity coefficients of fluorides renders this value only a rough approximation.

In earlier papers the theoretical significance and practical importance of the ionic entropies have been pointed out: we wish to call attention in this paper merely to the consistency which now exists in the values determined by wide varieties of methods. It should be noted that the checks obtained in Table I are, for almost every ion, more numerous than the cases listed under that ion. Thus, for example, if we use our accepted values for iodide, iodate, ferrous, ferric and sulfate, we can then calculate by five additional methods the entropy of silver ion. The maximum deviation from the mean (which includes also the error in the negative ion) is 0.8 e.u. It is also obvious from the data here presented that the third law of thermodynamics may be applied to salts of non-magnetic ions and their aqueous solutions without serious danger of errors due to zero point entropy or transitions at very low temperatures.

[1] Latimer and Buffington, J. Am. Chem. Soc. **48**, 2297 (1926).

[2] Latimer, J. Am. Chem. Soc. **43**, 818 (1921).

[3] See references to entropies listed in Table II.

TABLE I. *Summary of entropy calculations: $\Delta H°$ and $\Delta F°$ in calories per mole, $\Delta S°$ in calories per degree per mole. (The entropy data for the elements and compounds used in these calculations are summarized in Table II.)*

TABLE I. *Summary of entropy calculations: $\Delta H°$ and $\Delta F°$ in calories per mole. $\Delta S°$ in calories per degree per mole. (The entropy data for the elements and compounds used in these calculations are summarized in Table II.)*

Reaction	$\Delta H°_{298.1}$	$\Delta F°_{298.1}$	$\Delta S°_{298.1}$	
				$S°_{Cl^-}$
$\frac{1}{2}H_2+AgCl(s)=H^++Cl^-+Ag(s)$	−9600[4]	−5125[5]	−15.01	13.49
$HCl(g)=H^++Cl^-$	−17880[4d]	−8598[4d]	−31.14	13.52
$\frac{1}{2}H_2+\frac{1}{2}Cl_2(g)=H^++Cl^-$	−39940[4d]	−31373[4d]	−28.75	13.52
	−39940	−31367[6]	−28.77	13.50
				$S°_{Ag^+}$
$AgCl(s)=Ag^++Cl^-$	15980[7]	13297[8]	9.0	18.5
	15980	13329[9]	8.9	18.4
$Ag+\frac{1}{2}Cl_2(g)=Ag^++Cl^-$	−14330[8a]	−12890[8a]	−4.8	18.4
$Ag+H^+=Ag^++\frac{1}{2}H_2$	25540[10]	18448[6]	23.8	18.3
				$S°_{Hg_2^{++}}$
$2Hg(1)+2H^+=Hg_2^{++}+H_2$	40160[11]	36854[6]	11.1	16.5
$Hg_2Cl_2(s)=Hg_2^{++}+2Cl^-$	23740[12]	24446[11]	−2.4	16.2
				$S°_{Br^-}$
$\frac{1}{2}Br_2+\frac{1}{2}H_2=Br^-+H^+$	−28945[11]	−24577[8a]	−14.65	19.3
$AgCl(s)+Br^-=AgBr(s)+Cl^-$	−4457[8a]	−3461[8a]	−3.3	19.4
$AgBr(s)+\frac{1}{2}H_2=Ag(s)+H^++Br^-$	−5135[11]	−1673[6]	−11.6	19.5
				$S°_{I^-}$
$AgI(s)=Ag^++I^-$	26710[13]	21889[14]	16.2	25.4
$\frac{1}{2}H_2+\frac{1}{2}I_2=H^++I^-$	−13660[15]	−12361[6]	−4.3	25.2
$HI(g)=H^++I^-$	−19550[15]	−12676[6]	−23.0	26.5
$Ag(s)+\frac{1}{2}I_2(s)=Ag^++I^-$	11870[8a, 13]	6087[6]	19.4	24.9
				$S°_{Tl^+}$
$Tl+H^+=Tl^++\frac{1}{2}H_2$	935[15]	−7760[6]	29.2	28.5
$Tl+\frac{1}{2}Cl_2(g)=Tl^++Cl^-$	−38790[15]	−39105[7]	1.0	29.1
	−38930[16]	−39105	0.6	28.7
$TlCl=Tl^++Cl^-$	10125[17]	5086[11]	16.9	29.2
$Tl+\frac{1}{2}Br_2(1)=Tl^++Br^-$	−27990[11]	−32337[11]	14.5	28.4
$Tl+\frac{1}{2}I_2(s)=Tl^++I^-$	−12720[11]	−20082[11]	24.7	28.0
$TlI=Tl^++I^-$	17530[11]	9938[11]	25.5	28.6
				$S°_{NO_3^-}$
$TlNO_3=Tl^++NO_3^-$	9970[18]	1790[18]	27.4	36.9

Reaction	$\Delta H°_{298.1}$	$\Delta F°_{298.1}$	$\Delta S°_{298.1}$	
				$S°_{Ba^{++}}$
$Ba(NO_3)_2=Ba^{++}+2NO_3^-$	10200[19]	3200[19]	23.5	0.8
				$S°_{OH^-}$
$H_2O=H^++OH^-$	13329[20]	19122[11]	−19.4	−2.5
				$S°_{Ca^{++}}$
$Ca(OH)_2=Ca^{++}+2OH^-$	−3385[21]	6960[21]	−34.7	−11.4
				$S°_{Mg^{++}}$
$Mg(OH)_2=Mg^{++}+2OH^-$	−1180[15]	15410[22]	−55.6	−35.5
				$S°_{K^+}$
$KCl=K^++Cl^-$	4119[23]	−1207[24]	17.9	24.3
$KBr=K^++Br^-$	4910[25]	−1546[26]	21.7	24.8
$K+H^+=K^++\frac{1}{2}H_2$	−60340[11]	−67431[11]	23.8	24.7
				$S°_{S^=}$
$H_2+S(s)=2H^++S^=$	10040[11]	23450[11]	−45.0	−6.2
$H_2S(g)=2H^++S^=$	15300[11]	31290[11]	−53.6	−5.4
				$S°_{SO_4^=}$
$Ag_2SO_4=2Ag^++SO_4^=$	4210[41]	6722[41]	−8.4	2.8
$BaSO_4=Ba^{++}+SO_4^=$	5455[42]	13718[42]	−27.7	3.0
$CaSO_4\cdot 2H_2O=Ca^{++}+SO_4^=+2H_2O$	270[42]	6308[42]	−20.2	3.8
				$S°_{Na^+}$
$NaCl=Na^++Cl^-$	1019[27]	−2524[28]	11.9	15.7
	1019	−2161[28]	10.7	14.4
$NaBr=Na^++Br^-$	0[27]	−4231[28]	14.2	14.9
$Na+H^+=Na^++\frac{1}{2}H_2$	−57520[15]	−62588[11]	17.0	13.9
				$S°_{Pb^{++}}$
$Pb+2H^+=Pb^{++}+H_2$	−600[11]	−5877[29]	17.7	2.1
$Pb+Cl_2(g)=Pb^{++}+2Cl^-$	−80330[11]	−68567[11]	−39.5	2.4
$PbCl_2=Pb^{++}+2Cl^-$	5060[11]	6483[30]	−4.8	2.1
				$S°_{Fe^{++}}$
$Fe+Hg_2Cl_2(s)=Fe^{++}+2Cl^-+2Hg(1)$	−37500[11]	−32585[11]	−16.5	−28.0
$Fe+2TlCl(s)=Fe^{++}+2Cl^-+2Tl$	−3170[11]	5455[11]	−28.9	−27.6
$Fe+2H^+=Fe^{++}+H_2$	−20800[11]	−20240[11]	−1.9	−26.6
				$S°_{Fe^{+++}}$
$Fe^{++}+H^+=Fe^{+++}+\frac{1}{2}H_2$	11240[11]	17230[11]	−20.1	−63.1
$Fe^{+++}+Ag=Ag^++Fe^{++}$	14300[11]	12183[31]	43.9	−63.0

Reaction	$\Delta H°_{298.1}$	$\Delta F°_{298.1}$	$\Delta S°_{298.1}$	
				$S°_{Al^{+++}}$
$CsAl(SO_4)_2\cdot 12H_2O=Cs^++Al^{+++}+2SO_4^=+12H_2O$	13560[32]	12910[32]	2.18	−71.7
				$S°_{Li^+}$
$Li+H^+=Li^++\frac{1}{2}H_2$	−66380[33]	−68248[33]	6.2	1.8
				$S°_{Rb^+}$
$Rb+H^+=Rb^++\frac{1}{2}H_2$	−61210[33]	−67473[33]	21.0	22.8
				$S°_{Cu^{++}}$
$Cu+2H^+=Cu^{++}+H_2$	16640[33]	15912[33]	2.4	−21.0
				$S°_{Cd^{++}}$
$Cd+2H^+=Cd^{++}+H_2$	−16510[33]	−18348[33]	6.2	−12.7
				$S°_{Sn^{++}}$
$Sn+2H^+=Sn^{++}+H_2$	−2390[33]	−6276[33]	13.0	−5.9
				$S°_{Hg^{++}}$
$Hg+2H^+=Hg^{++}+H_2$	41590[33]	39679[33]	6.4	−6.5
				$S°_{Zn^{++}}$
$Zn+2H^+=Zn^{++}+H_2$	−36720[33]	−34984[33]	−5.8	−27.2
				$S°_{ClO_3^-}$
$KClO_3=K^++ClO_3^-$	10120[34]	12774[34]	29.7	39.3
				$S°_{BrO_3^-}$
$Ba(BrO_3)_2\cdot H_2O=Ba^{++}+2BrO_3^-+H_2O$	15360[35]	7170[35]	26.5	38.7
$KBrO_3=K^++BrO_3^-$	9540[36]	16900[36]	26.3	37.4
				$S°_{IO_3^-}$
$AgIO_3=Ag^++IO_3^-$	13200[37]	10200[37]	10.1	27.7
$KIO_3=K^++IO_3^-$	6340[36]	1770[36]	15.3	26.9
				$S°_{ClO_4^-}$
$KClO_4=K^++ClO_4^-$	12115[38]	2690[38]	31.6	43.1
				$S°_{C_2O_4^=}$
$CaC_2O_4\cdot H_2O=Ca^{++}+C_2O_4^=+H_2O$	5090[39]	11790[39]	−22.5	9.3
				$S°_{CO_3^=}$
$CaCO_3+C_2O_4^=+H_2O=CaC_2O_4\cdot H_2O+CO_3^=$	−7460[11]	−306[11]	−24.0	−13.1
$C+{}^3/_2O_2+H_2=2H^++CO_3^=$	−161100[11]	−125760[11]	−118.5	−12.5
$CaCO_3=Ca^{++}+CO_3^=$	−2780[40]	10922[40]	−46.0	−12.6

[4] (a) Noyes and Ellis, J. Am. Chem. Soc. **36**, 1969 (1914); (b) Harned and Brumbaugh, J. Am. Chem. Soc. **44**, 2729 (1922); (c) Butler and Robertson, Proc. Roy. Soc. **A125**, 694 (1929); (d) Rossini, Bur. Standards J. Research **9**, 679 (1932). The average of these values is −9600 with a maximum deviation of 48 cal.

[5] Randall and Young, J. Am. Chem. Soc. **50**, 989 (1928).

[6] Gerke, Chem. Rev. **1**, 377 (1925).

[7] Lange and Fuoss, Zeits. f. physik. Chemie **125**, 431 (1927).

[8] (a) Randall and Spencer, unpublished data; (b) Gerke's value for $Ag-Ag^+$ electrode, reference 6.

[9] Randall and Young, reference 5, data for silver chloride electrode with reference (8b).

[10] Combination of data from reference 8(a) and Rossini, reference 4(d).

[11] *International Critical Tables.*

[12] Kohlrausch, Zeits. f. physik. Chemie **64**, 129 (1908), temperature coefficient of solubility data.

[13] Lange and Shibata, Zeits. f. physik. Chemie **A149**, 465 (1930).

[14] The solubility of AgI has been taken as $1.05\times10^{-8}M$ from a survey of various values in the literature. The potential of the silver-silver iodide electrode by Jones and

TABLE II. *Summary of entropy values used in the calculation of Table I. Values in calories per degree per mole.*

Substance	$S°_{298.1}$	Substance	$S°_{298.1}$
$Ba(BrO_3)_2 \cdot H_2O$	68.7[35]	O_2	49.0[51]
$Ba(NO_3)_2$	51.1[19]	K	16.5[11]
$BaSO_4$	31.5[42]	KBr	22.5[11]
Br_2	36.8[43]	$KBrO_3$	35.6[36]
Cd	12.3[11]	KCl	19.9[52]
$CaCO_3$	22.1[11]	$KClO_3$	34.2[34]
$Ca(OH)_2$	18.2[39]	$KClO_4$	36.1[38]
$CaC_2O_4 \cdot H_2O$	37.3[39]	KIO_3	36.2[35]
$CaSO_4 \cdot 2H_2O$	46.4[42]	Rb	17.4[11]
C	1.4[11]	Ag	10.0[53]
$CsAl(SO_4)_2 \cdot 12H_2O$	163.8[32]	AgBr	25.6[54]
Cl_2	53.3[44]	AgCl	23.0[54]
Cu	7.8[11]	AgI	27.6[49]
H_2	31.2[45]	$AgIO_3$	36.0[37]
HCl	44.7[46]	Ag_2SO_4	47.8[41]
HI	49.5[47]	NaCl	17.2[30]
H_2O	16.9[48]	NaBr	20.1[2]
H_2S	48.2[49]	Na	12.5[11]
I_2	27.9[11]	S	7.6[11]
Fe	6.5[11]	Tl	14.9[11]
Pb	15.6[11]	TlBr	28.9[11]
$PbCl_2$	33.9[11]	TlCl	25.8[11]
Li	7.6[11]	TlI	28.6[11]
$Mg(OH)_2$	15.1[50]	$TlNO_3$	38.1[18]
Hg	18.3[11]	Sn	12.3[11]
Hg_2Cl_2	45.6[11]	Zn	9.8[11]

TABLE III. *Entropies of aqueous ions at 298.1°K. Values in calories per degree per mole.*

Li^+	1.8	Fe^{++}	-27.4 ± 0.7
Na^+	14.7 ± 1.0	Fe^{+++}	-63.0
K^+	24.6 ± 0.5	Al^{+++}	-71.7
Rb^+	22.8	F^-	-5.0
Tl^+	28.6 ± 0.3	Cl^-	13.5 ± 0.1
Hg_2^{++}	16.4 ± 0.5	Br^-	19.4 ± 0.4
Ag^+	18.4 ± 0.2	I^-	25.7 ± 0.7
Mg^{++}	-35.5	NO_3^-	36.9
		ClO_4^-	43.1
Ca^{++}	-11.4	ClO_3^-	39.3
Ba^{++}	0.8	BrO_3^-	37.7 ± 1.0
Cu^{++}	-21.0	IO_3^-	27.1 ± 1.0
Zn^{++}	-27.2	OH^-	-2.5
Cd^{++}	-12.7	CO_3^{--}	-12.7 ± 0.5
Sn^{++}	-5.9	SO_4^{--}	3.5 ± 0.5
Hg^{++}	-6.5	$C_2O_4^{--}$	9.3
Pb^{++}	2.2 ± 0.2	S^{--}	-5.8 ± 1.0

Kasplan, J. Am. Chem. Soc. **50**, 1863 (1928) gives a value of 21,887 for this free energy.

[15] *International Critical Tables*, corrected to 25°C.

[16] *International Critical Tables*, using the sum of the heats of formation instead of the direct determination.

[17] (a) Thomsen, *Thermochemistry*, p. 52, Longmans Green and Co., N. Y., 1908. (b) Butler and Hiscocks, J. Chem. Soc. 2554 (1926). We have used a mean of these values after correcting for dilution and temperature effects.

[18] Latimer and Ahlberg, J. Am. Chem. Soc. **54**, 1903 (1932).

[19] Latimer and Ahlberg, Zeits. f. physik. Chemie **A148**, 468 (1930).

[20] Rossini, Bur. Standards J. Research **6**, 847 (1931).

[21] Latimer, Schutz and Hicks, J. Am. Chem. Soc. **55**, 971 (1933).

[22] Kline, J. Am. Chem. Soc. **51**, 2093 (1929), gives 5×10^{-12} as the solubility product of $Mg(OH)_2$.

[23] Lange and Monheim, Zeits. f. physik. Chemie **A150**, 349 (1930).

[24] Pearce and Nelson, J. Am. Chem. Soc. **54**, 3544 (1932) give $\gamma \pm = 0.576$ at saturation, 4.81*M* KCl.

[25] *Landolt Börnstein Tabellen*, corrected to 25°C.

[26] (a) Seidell, *Solubility of Inorganic and Organic Compounds*, D. Van Nostrand Co., N. Y. (1919). (b) *Landolt Börnstein, Tabellen*, II Ergänzungband gives $\gamma \pm$ as 0.627 for 4*M* KCl. Extrapolating to saturated solution we find $\gamma \pm 0.65$.

[27] Wüst and Lange, Zeits. f. physik. Chemie **A116**, 190 (1925).

[28] Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill, N. Y. (1923).

[29] Fromherz, Zeits. f. physik. Chemie **A153**, 376 (1931).

[30] *Landolt Börnstein Tabellen.*

[31] Noyes and Beam, J. Am. Chem. Soc. **34**, 1016 (1912).

[32] Latimer and Greensfelder, J. Am. Chem. Soc. **50**, 2202 (1928).

[33] These data have been obtained from various sources including the *International Critical Tables* and *Landolt Börnstein Tabellen.* Special reference should also be made to the work of Richards and co-workers.

[34] Latimer, Schutz and Hicks, J. Am. Chem. Soc. (in press).

[35] Greensfelder and Latimer, J. Am. Chem. Soc. **50**, 3286 (1928). These values have been recalculated and a large error in the graphical integration of the entropy of $Ba(BrO_3)_2 \cdot H_2O$ has been corrected. The correct value is 68.7.

[36] Ahlberg and Latimer, J. Am. Chem. Soc. (in press).

[37] Greensfelder and Latimer, J. Am. Chem. Soc. **53**, 3813 (1931). The ΔH value given in this paper has been recalculated from the solubility data.

[38] Latimer and Ahlberg, J. Am. Chem. Soc. **52**, 549 (1930).

[39] Latimer, Schutz and Hicks, J. Am. Chem. Soc. **55**, 971 (1933).

[40] Backström, J. Am. Chem. Soc. **47**, 2432 (1925).

[41] Latimer, Hicks and Schutz, J. Chem. Phys. **1**, 424 (1933).

[42] Latimer, Hicks and Schutz, J. Chem. Phys. **1**, 620 (1933).

[43] Latimer and Hoenshel, J. Am. Chem. Soc. **48**, 19 (1926).

[44] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1741 (1932).

[45] Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

[46] Giauque and Wiebe, J. Am. Chem. Soc. **50**, 101 (1928).

[47] Giauque and Wiebe, J. Am. Chem. Soc. **51**, 1441 (1929).

[48] Giauque and Ashley, Phys. Rev. **43**, 1 (1933).

[49] Kelley, U. S. Bureau of Mines Bull. 350 (1932).

[50] Giauque and Archibald, unpublished data.

[51] Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).

[52] Nernst, Ann. d. Physik **36**, 395 (1911).

[53] Giauque and Meads, unpublished data.

[54] Eastman and Milner, J. Chem. Phys. **1**, 444 (1933).

On the Statistical Basis of the Theory of Electrolytes

OTTO HALPERN, *Physics Department, New York University, University Heights*

(Received December 14, 1933)

In the following paper the author investigates how far the various statistical-thermodynamic methods hitherto proposed are suitable for application to strong electrolytes. The significance of the ionic radius is, in many instances, far more important than has hitherto been assumed. When the influence of the ionic radius is negligible conditions are derived from dimensional considerations which considerably restrict the functional form of the free energy. Furthermore, proceeding from conditions of integrability, thermodynamics appreciably limits the number of possible expressions for the ionic potential. The disregarding of these limitations has been responsible for certain paradoxes in the literature on this subject. A new fluctuation formula for the electric potential of the ions is derived and conclusions are drawn from it as to the correctness of existing theories. In connection with this last a deduction proposed by Fowler is reviewed. Kramers' theory of electrolytes is tested with respect to its agreement with the theorems here developed. Finally, a review of the statistical and thermodynamical basis of Bjerrum's theory of ionic association is presented.

1. INTRODUCTORY REMARKS

UNEXPECTED progress has been made in the theory of strong electrolytes in the course of the decade since Debye's theory was first put forward. Whereas (assuming the correctness of Debye's deduction for the mean ionic potential) the thermodynamic part was practically disposed of, Debye's conception of the ionic cloud, on the other hand, gave rise to the discovery and interpretation of a number of effects in the field of conductivity. The knowledge thus gained must be regarded as an addition of permanent value to this field.

The basis for this development is provided by Debye's method of calculating the mean ionic potential. That this method does not follow directly from the recognized laws of statistics but must, on the contrary, first be justified by means of statistical principles, has already been emphasized by so many authors that it is hardly necessary to go further into this point at present. The matter lies about as follows: because of the repeatedly observed agreement in the field of dilute aqueous solutions between Debye's theory and experiment a great variety of methods has been tried to vindicate this agreement in theory. The efforts made in this direction are essentially divisible into three groups. To the first of these belong the investigations carried out by Fowler[1] and Kramers[2] which proceeded from the rigorous phase integral of Gibbs' canonical ensemble and from this aimed at obtaining Debye's formulas. The second group contains first and foremost an important inquiry by Gronwall, La Mer and Sandved[3] who proceed from the same differential equation as Debye but aim at putting it from the start on a stricter mathematical basis by calculating the higher approximations, a procedure which would be unfeasible on principle if the ionic radius were disregarded. Finally, the third group is composed of an investigation by Bjerrum[4] and of subsequent work following the program outlined in it. In this were introduced, by way of completing Debye's mode of approach, the conceptions of ionic association which are to be explained below.

The result of these investigations as given by the authors themselves, can in its main features be summed up as follows: A concentration can always be found below which the Debye theory retains its validity as a limiting law. For higher concentrations deviations from Debye's limiting law enter which vary according to the different authors. In this connection the Debye limiting law is defined by the statement that the excess

[1] R. H. Fowler, *Statistical Mechanics*, Chapters 8 and 13.

[2] H. A. Kramers, *Proc. Amst. Akad. Sci.* **30**, 145 (1927).

[3] T. H. Gronwall, V. K. La Mer and K. Sandved, Phys. Zeits. **29**, 358 (1928).

[4] N. Bjerrum, Copenhagen Akad. Inst. fys. Medd. **7**, 9 (1926).

free energy of an ionic solution is given by the formula

$$F = -\sum_i N_i \epsilon_i^2 \kappa / 3D, \qquad (1)$$
$$\kappa = (4\pi \sum_i N_i \epsilon_i^2 / DkTV)^{\frac{1}{2}}.$$

The symbols entering into this formula require no further explanation.

It is the purpose of the present investigation to test in the first place the correctness of these results, secondly to show how far it is possible to draw from general properties (conditions of dimension and integrability, etc.) conclusions which must be valid for all theories without exception, and finally to test the validity of certain corollaries of the theory with the aid of general thermodynamic conditions.

2. Dimensional Considerations and Thermodynamic Conditions of Integrability

We shall consider a solution composed of various ions of charge ϵ_i. The number of ions of the i-th group will be denoted by N_i, the total number of all ions by N, the total volume of the solution by V, the dielectric constant by D and the radii of the ions of the i-th kind by a_i. The difficulty inherent in the use of the macroscopic dielectric constant for the treatment of the microscopic forces between the ions has already been emphasized by several authors and will not be gone into here, since we are merely able to recognize its existence but not to overcome it.

Between the ions act the Coulomb forces and repelling forces of the van der Waals type, which prevent the uniting of two opposite charges. We have already partially taken these forces into account by the introduction of ionic radii. The electrical potential energy of two ions of the i-th and k-th kinds is then

$$\epsilon_i \epsilon_k / D r_{ik},$$

in which r_{ik} denotes the instantaneous distance between the two ions. For the purpose of the following considerations we shall assume the ions to be consecutively numbered from 1 to N, and the i-th ion to have the charge ϵ_i. There are then, accordingly, groups of N_i ions present which all have one and the same charge ϵ_i, although it is not necessarily to be assumed that any two ions in the solution have the same charge. The total excess free energy of the ionic solution, insofar as it is due to the forces between the ions, is then known to be given by Gibbs' phase integral

$$e^{-(F/kT)} V^N = \int dx_1 \cdots dz_N e^{-E/kT}. \qquad (2)$$

In E both the Coulomb and the van der Waals forces are to be included. If the potential energy of the van der Waals forces (short range forces) be put down as E_W, then E equals

$$E = E_C + E_W = E_W + \tfrac{1}{2} \sum\sum \epsilon_i \epsilon_k / D r_{ik}. \qquad (3)$$

In this expression for the potential energy the proper electric energy $\epsilon_i^2/2Da_i$ of each ion is omitted as being an uninteresting constant. If E be written in the form

$$E = E_W + \tfrac{1}{2} \sum_i \epsilon_i \psi_i, \qquad (4)$$

then

$$\psi_i = \sum_k \epsilon_k / D r_{ik} \qquad (5)$$

denotes the instantaneous potential produced by all other ions at the position of the i-th ion.

In any electrostatic system the relation[5]

$$\psi_i = \partial E_C / \partial \epsilon_i \qquad (6)$$

which follows directly from (3) and (5) is valid. The mean value of the potential $\overline{\psi_i}$ then results on taking the statistical mean value of the expression $\partial E_C / \partial \epsilon_i$. This statistical mean value is obtained by differentiating both sides of (2) with respect to ϵ_i. Thus

$$\overline{\psi_i} = \frac{\partial F}{\partial \epsilon_i} = \frac{\int dx_1 \cdots dz_N (\partial E_C / \partial \epsilon_i) e^{(F - E_W - E_C)/kT}}{V^N}. \qquad (7)$$

From this follows at once by a second differentiation the fundamental relation

$$\partial \overline{\psi_i} / \partial \epsilon_k = \partial \overline{\psi_k} / \partial \epsilon_i. \qquad (8)^*$$

In the absence of van der Waals forces (vanishing ionic radius) the phase integral clearly diverges, since all ions of opposite sign simply neutralize each other. A finite ionic radius (presence of van der Waals forces) is thus of decisive

[5] The method employed at this point and subsequently is closely connected with that used in an earlier investigation. Cf. Gross and Halpern, Phys. Zeits. **26**, 403 (1925).

* All differentiations with respect to ϵ_i are, of course, carried out at constant temperature; the resulting relations for $\overline{\psi}$ therefore refer to *isothermal* properties of the ionic potentials.

importance for the statistical problem. *There is therefore no concentration at which the value of the free energy is independent of the ionic radius (i.e., of the magnitude of the van der Waals forces). It is merely possible, as shown by experiment, to find cases in which, for a given range of values of the ionic radius, the free energy is not appreciably dependent on the actual value of this ionic radius.* In such cases we can write, *as an approximation*

$$\overline{E}=\overline{E}_C=\tfrac{1}{2}\sum_i \epsilon_i\psi_i \qquad (3a)$$

and thus obtain by means of (7) the relation

$$\overline{E}=F-kT(\partial F/\partial(kT))=\tfrac{1}{2}\sum_i(\partial F/\partial\epsilon_i)\epsilon_i \qquad (9)$$

or, by a simple transformation ($\eta_i=\epsilon_i^2$),

$$F=kT\frac{\partial F}{\partial(kT)}+\sum_i\eta_i\frac{\partial F}{\partial\eta_i}. \qquad (10)$$

The solution of this Eulerian partial differential equation is

$$F=kTG(\eta_i/kT), \qquad (11)$$

in which G signifies an *arbitrary function* of the N arguments η_i/kT. G must have the dimension 0; since η_i/kT is of the dimension of a length, G can only be made dimensionless by the introduction of the factor $V^{-\frac{1}{3}}$, so that Eq. (11) takes the form

$$F=kTG(\eta_i/kTV^{\frac{1}{3}}). \qquad (12)$$

This dimensional equation previously has been obtained by O. Klein[6] using a statistical method.

These dimensional considerations may, however, be carried considerably further: As is readily seen from (3), E is a *symmetrical function* of the ϵ_i. This symmetry must accordingly also be valid for F. We may therefore add to (12) the further condition that G depends *symmetrically* upon the arguments η_i.

Further, as long as we ignore surface phenomena, the free energy, as always in thermodynamics, must be proportional to the total number of the ions, so that the N_i enter in the expression for F only in the form $N_if(N_i/V)$. For the following considerations it is of *decisive importance* to observe that F does *not* contain the number N_i of ions of the i-th class *explicitly* but only through the fact that precisely N_i ions have all the same charge ϵ_i. We thus obtain a further limitation, since F has to be of the form

$$F=\sum_i\frac{\eta_i}{V^{\frac{1}{3}}}H_i\left(\frac{\eta_l}{kTV^{\frac{1}{3}}}\right)\equiv\sum_iN_i\eta_iK\left(\frac{N_i}{V}\right), \qquad (13)$$

$$H_i=H_k \quad \text{(on account of symmetry!)}.$$

This limitation might appear at first sight to be of subsidiary importance, but this is by no means the case.[7]

It must once more be emphasized that all considerations which disregard the ionic radius can not be of general validity but are only justified when it is known that the ionic radius lies within a certain range and that the results are practically independent of its actual value.

3. Applications of the Relations (8) and (13)

Let it be first assumed, as is done in the investigations of a number of authors, that F is only a function of the *ionic strength*. This is defined by the expression

$$F=\sum_i N_i\epsilon_i^2f(\textstyle\sum_iN_i\epsilon_i^2), \qquad (14)$$

$$\textstyle\sum_i N_i\epsilon_i^2=\text{ionic strength}.$$

This assumption is permissible, since according

[6] O. Klein, Medd. fr. K. Vet. Nobelinst. **5** (1919). A derivation of this same equation given by P. van Rysselberghe, J. Chem. Phys. **1**, 205 (1933), with the aid of the virial theorem can not be regarded as satisfactory, since in the derivation (Cf., e.g., the transition from (12) to (14) and from (21) to (23)) quantities are treated as independent where as they are actually dependent on the variable of differentiation.

[7] One might cast doubt upon the correctness of this argument by referring to the fact that perhaps the number N enters into the expression for the free energy not only by the number of the charge carriers but also through the volume V which is available to all the particles. This, however, is not the case: Let us assume that the N_i enter in some way into the expression for F not only through the ϵ_i but also through V. Let us then compare the excess free energies of two solutions, one containing N ions and the other M additional ions carrying infinitesimally small charges (in the limiting case the charge 0). The excess free energies must then obviously be equal since the ions with the charge 0 can have no effect. They would be *unequal* however if V were to contain the number of ions as a factor. It must be borne in mind that we are here dealing only with excess free energies as defined above. Failure to notice this fact is responsible for a conflicting result obtained by Kramers (cf. §5 of this note) which therefore must be held to be invalid.

to it F becomes a symmetrical function of ϵ_i^2. In order to give (14) the form (13) we write

$$F=\frac{\sum_i N_i\epsilon_i^2}{V^{\frac{1}{3}}}H\left(\frac{\sum_i N_i\epsilon_i^2}{kTV^{\frac{1}{3}}}\right). \tag{15}$$

It will be seen at once that (15) satisfies the condition (13), only when F is of the form[8]

$$F=C\sum_i(N_i\epsilon_i^2/D)(\sum_i N_i\epsilon_i^2/DkTV)^{\frac{1}{3}}. \tag{16}$$

$$C=\text{pure number.}$$

From general dimensional considerations therefore we obtain the following result: *Assuming that the free energy is a function merely of the ionic strength and assuming further that the ionic radius lies in a range in which its influence may be disregarded, then a limiting law for the free energy is always valid and this law can differ from that of Debye only by a numerical factor.*

A similar conclusion can be drawn in a related case. Suppose it is known, for example, that the mean potential $\overline{\psi}_i$ is of the form $\overline{\psi}_i=\epsilon_i f_i$, in which f_i denotes any symmetrical function of the η_l (possibly with the omission of the variable η_i). The condition (8) then leads to the relation

$$\epsilon_i\partial f_i/\partial\epsilon_k=\epsilon_k\partial f_k/\partial\epsilon_i. \tag{17}$$

This can only hold true when f_i contains the ϵ_l in the combination

$$f_i=f_k=f(\sum_l\epsilon_l^2). \tag{18}$$

For, in this case,

$$2\epsilon_i\epsilon_k f'=2\epsilon_k\epsilon_i f', \tag{19}$$

in which the prime denotes differentiation with respect to the argument $(\sum\epsilon_l^2)$. From this point on the argument runs as above.

A considerable number of proposed theoretical formulae do *not* satisfy the general conditions here given or do so only in special cases obtained by artificial restrictions on the parameters, restrictions for which no physical reasons whatsoever can be assigned. Thus, for example, the expression previously given by Debye for the mean potential of an ion, as a function of the ionic radius,

$$\overline{\psi}_i=-\epsilon_i\kappa/D(1+\kappa a_i),$$

is only in agreement with (8) if $a_i=a_k$ be valid. The same argument applies to the more consistent method of integration of Debye's differential equation given by Gronwall, La Mer and Sandved, although it becomes clear, when the higher approximations are taken into consideration, that *even in the case of equal radii* the condition (8) is in general not fulfilled, *unless all the ions carry the same charge.* Thus, for example, Gronwall, La Mer and Sandved obtain for the potential of an ion originating from a uni-divalent electrolyte the expression

$$\overline{\psi}_i=\sum_1^\infty{}_m(\epsilon_i^{2m-1}/a_i^m)\varphi_m, \tag{20}$$

in which $\varphi_m(\epsilon_i^2)$ denotes a symmetrical function which is of no importance for our further deductions. It will be seen at once that (20) no longer satisfies the condition (8) in higher approximations, since if we write $\overline{\psi}_i$ in the form

$$\overline{\psi}_i=\sum_1^\infty{}_m\psi_i^{(m)}$$

the relation

$$\partial\psi_i^{(m)}/\partial\epsilon_k=\partial\psi_k^{(m)}/\partial\epsilon_i$$

is no longer valid for $m>1$. In this connection it must be emphasized that the calculation according to Gronwall, La Mer and Sandved is more consistent and that it alone gives a justification of Debye's method of calculation. The fact that the thermodynamic integrability conditions can not be satisfied points to serious inherent weaknesses of the theory which only accidentally do not become manifest in the first approximation (with ionic radii equal). All theoretical attempts to treat the case of unequal ionic radii on the basis of the Debye theory, have, so far as the author knows, led to formulas which fail to satisfy the integrability condition (8).

For practical purposes this limitation has been of no great importance, since ionic radii have been introduced, at least in aqueous solutions, only for the purpose of correction, and differences between individual ionic radii lie outside the range of accuracy of the theory. But it must be observed, in order to appreciate the argument, that the equality of the ionic radii enforced by thermodynamics is in fact a physically absurd limitation.

[8] It follows from (2) and (3) that E and therefore F contain the ϵ only in the combination ϵ^2/D.

A paradox emphasized in the paper by Gronwall, La Mer and Sandved[9] quoted above also finds its explanation in this manner. If we wish to calculate the free energy of an ionic solution from the given potentials $\overline{\psi_i}$, it is necessary on account of (7) to carry out the integration of the following system of N partial differential equations for the one unknown quantity F

$$\partial F/\partial \epsilon_i = \overline{\psi_i} \qquad (21)$$

$$(i = 1, 2 \cdots N).$$

Since for $\epsilon_i = 0$ the free energy is equal to 0, we can in every case take $\epsilon_i = 0$ as the lower limit of integration. The upper limit of integration is given of course by $\epsilon_i = \epsilon_i$. Since we are here dealing with N independent variables it is possible to carry out the integration in any number of ways. The Eqs. (21) and (8) invariably lead to the same result, since it is clear that (8) expresses the necessary and sufficient conditions for the integrability of (21). If (8) is not fulfilled then this is no longer the case. Gronwall, La Mer and Sandved carried out the integration by causing (at least for symmetrical electrolytes of uniform ionic radius) all ionic charges to increase at an equal rate so that during the process of integration all ions had the same charge at any one time. These authors thus maintained, during the integration process, equality of all charges concerned, a condition on which the fulfillment of (8) had been shown to depend. Their result differs from that obtained by H. Mueller, since the latter carried out a different method of integration. He began by causing the charge of the k-th ion to increase from 0 to ϵ_k, while the charges of the other ions were kept constant. During this process there were thus present in the solution ions "of different valencies," so that the integrability conditions (8) were not fulfilled; the deviation of his result from that of Gronwall, La Mer and Sandved, in whose work the integrability condition was (artificially) fulfilled, is thus readily explained.[10]

[9] Gronwall, La Mer and Sandved, Phys. Zeits. **29**, 367 (1928).

[10] The significance of the integrability condition and its use to explain the charge paradox has already formed the subject of a communication previously made, as a preliminary statement, by the present author. Cf. Phys. Rev. **43**, 495 (1933).

4. Fluctuations of Potential

Debye's methods of calculation, which have proved successful in so many instances, consist, as is well known, in determining the distribution of the charge in the vicinity of a particular ion by combining the Poisson equation with a somewhat free analog of the e-theorem of Boltzmann.

$$\Delta\overline{\psi} = -\epsilon\pi\rho/D = -(\epsilon\pi/D)\sum \rho_0^{(i)} e^{-\epsilon_i\overline{\psi}/kT}. \qquad (22)$$

This use of the Boltzmann theorem urgently requires justification by strict statistical principles. If the potential, which also occurs as argument of the exponential function, were determined solely by the particular ion, then this application would be justified. In the case with which we are here concerned it is precisely the contributions of the other ions to this potential which are of decisive importance and for these the simple formulation of the Boltzmann theorem here introduced is not valid. These objections were already raised some time ago by a number of authors and the investigations of Kramers and Fowler, mentioned in the introduction to this paper, aimed primarily at dealing therewith.

As to the magnitude of the error introduced by the use of the Boltzmann theorem, no theoretical statement has hitherto been possible although some information on this point can be obtained with the aid of a strictly valid fluctuation formula for the potential. For this purpose we proceed from the relations (2), (4), (6) and (7) which are strictly valid even in the case of the presence of van der Waals forces, and obtain by differentiation of (7) with respect to ϵ_i. the relation

$$V^N \frac{\partial\overline{\psi_i}}{\partial\epsilon_i} = \int dx_1 \cdots dz_N \frac{\partial}{\partial\epsilon_i}\left\{\frac{\partial E_C}{\partial\epsilon_i} e^{(F-E_W-E_C)/kT}\right\}. \qquad (23)$$

The expression on the right, however, becomes simplified in view of (Cf. (6) and (7))

$$\partial^2 E_C/\partial\epsilon_i^2 = 0, \qquad \partial F/\partial\epsilon_i = \overline{\psi_i}$$

to

$$V_N \frac{\partial\overline{\psi_i}}{\partial\epsilon_i} = \frac{1}{kT}\int dx_1 \cdots dz_N e^{(F-E_W-E_C)/kT}$$

$$\times(\psi_i\overline{\psi}_i - \psi_i^2) = V^N(1/kT)(\overline{\psi_i^2} - \overline{\psi_i}^2). \qquad (24)$$

In this connection, as is once more emphasized, ψ_i is merely the potential produced by the other

ions at the position of the i-th ion. For the quantitative evaluation of this fluctuation formula it is necessary to know the expression for $\partial\overline{\psi_i}/\partial\epsilon_i$. For our purposes it is perfectly sufficient to regard it as empirically given, by osmotic or activity measurements. Then, as a close approximation, we have in dilute solutions

$$\partial\overline{\psi_i}/\partial\epsilon_i=\overline{\psi_i}/\epsilon_i$$

and therefore

$$\overline{\psi_i^2}-\overline{\psi_i}^2=-(kT/\epsilon_1)\overline{\psi_i}. \tag{25}$$

Now Debye's theory has hitherto been applied to aqueous solutions practically only for such ranges in which

$$\epsilon_i\overline{\psi_i}/kT\ll 1. \tag{26}$$

Indeed the estimates to be discussed later, as to the range of validity of the Debye formulas, furnished as a necessary limitation precisely the relation (26). In this case, however, we see from the *strictly valid* fluctuation formula that the potential produced by all other ions exhibits fluctuations which are very great compared with its mean value. Moreover this ratio—and this is perhaps the most important point in the present analysis—is made not better but worse when we pass over to smaller concentrations. For then $\overline{\psi_i}^2$ approaches 0 as N/V, but $\overline{\psi_i^2}$ only as $(N/V)^{\frac{1}{2}}$. If possible at all, it is thus only at higher concentrations that the use of the mean value of ψ in (22) can to some extent be justified; but then the van der Waals forces must be explicitly taken into account.

The higher fluctuations of ψ_i, ψ_i^3, etc., can be determined in an analogous manner; since, however, they do not lead to further restricting conditions, they will not here be explicitly given.*

5. Remarks on the Investigations by Kramers and Fowler

The result arrived at in the preceding paragraphs conflicts with a relation deduced by Fowler also from statistical mechanics, according to which it would appear that at sufficiently low concentrations, Debye's method of combining the Poisson equation and the Boltzmann theorem was correct. Fowler[1] derives the following relation:

$$\epsilon_m\Delta\psi_i+4\pi\bar{\rho}\epsilon_m/D = -\frac{1}{kT}\left\{\sum_{xyz}\left[\overline{\left(\frac{\partial W}{\partial x}\right)^2}-\left(\frac{\partial W_m}{\partial x}\right)^2\right]\right. \tag{27}$$

The left side of this equation requires no further explanation; for the exact meaning of the density $\bar{\rho}$ here introduced, reference should be made to Fowler's own arguments. W denotes the energy which the m-th ion situated at the point x, y, z assumes, under the influence of the particular ion and of all other ions, $\sum(\partial W/\partial x)^2$ the square of the gradient of this energy, and W_m the mean value of W. In Debye's theory the right side of (27) is made equal to 0. This is permissible according to Fowler, provided the terms on the right side are small compared with those on the left side. He shows by explicit calculation that $\sum_{xyz}(\partial W_m/\partial x)^2 1/kT$ is, in fact, sufficiently small when

$$\epsilon_m\overline{\psi_i}/kT\ll 1$$

holds. This implies that in Fowler's opinion we may, in fact, make the right-hand side equal to 0, at very low concentrations.

In this connection, however, it has not been taken into consideration that $\overline{(\partial W/\partial x)^2}$ in view of

$$\overline{\left(\frac{\partial W}{\partial x}-\frac{\partial W_m}{\partial x}\right)^2}=\overline{\left(\frac{\partial W}{\partial x}\right)^2}-\left(\frac{\partial W_m}{\partial x}\right)^2>0$$

is invariably greater than $(\partial W_m/\partial x)^2$ and in the present case even becomes of a higher order of magnitude. This can be demonstrated in the following manner. $\partial W/\partial x$ denotes the instantaneous force exerted in the x-direction upon a charge ϵ_m at the point x, y, z. The mean value of the expression

$$(1/kT\epsilon_m^2)\sum_{xyz}(\partial W/\partial x)^2$$

is thus equal to the mean of the square of the field strength at the point occupied by the charge. The order of magnitude of this quantity $\overline{(\vec{E})^2}$ can be calculated from the general relation

$$A=(DV/8\pi)\overline{(\vec{E})^2}, \tag{28}$$

in which A denotes the free electric energy of the solution. This free electric energy contains *as*

* Similar applications of the fluctuation-formulae can be made to the problem of electric and magnetic polarizability (Clausius-Mosotti relation and Lorentz's inner field). Cf. a preliminary note of the present author, Phys. Rev. **40**, 134 (1932).

largest term the *proper energy* of the ions which for spherical ions is approximately given by

$$A = \sum N_i \epsilon_i^2 / 2Da. \tag{29}$$

We thus obtain

$$\frac{1}{kT}\sum\overline{\left(\frac{\partial W}{\partial x}\right)^2} = \frac{\epsilon_m^2}{kT}\overline{(\vec{E})^2} = \frac{8\pi\epsilon_m^2 A}{DVkT}$$
$$= \frac{8\pi\epsilon_m^2}{DkTV}\sum\frac{N_i\epsilon_i^2}{2Da} = \kappa^2\frac{\epsilon_m^2}{2aD}. \tag{30}$$

The other terms in the free electric energy A, due to the interaction of the ions, will be disregarded *in this connection*, since we have already shown in the preceding paragraph that they are of an appreciable order of magnitude. At all events, provided the concentrations concerned are not too high, the following holds:[11]

$$|\kappa^2\epsilon_m\bar{\psi}| = \epsilon_m^2\kappa^3/D \ll 1/kT\sum_{xyz}\overline{(\partial W/\partial x)^2}$$
$$= \epsilon_m^2\kappa^2/2aD \tag{31}$$

for all $\kappa \ll 1/a$. This shows again that it is not justifiable to make the right side equal to 0 and that going to lower concentrations by no means improves matters.

Kramers has attempted to evaluate the Gibbs phase integral directly by a very ingenious method. Unfortunately the assumptions and omissions made in the course of the integration can hardly be estimated in their effect on the final result. We shall, therefore, not enter into a discussion of the various details and shall content ourselves with drawing attention to only two points of general significance. As the result of his calculations, Kramers obtains for the free energy an expression of the form

$$F = -\sum_i N_i\epsilon_i^2(\kappa/3D + C\kappa^2 + \cdots). \tag{32}$$

As will be seen, the free energy is here only a function of κ and therefore of the ionic strength; in spite of this other terms occur in (32) besides those giving the limiting law (1). This is contradictory to the rigorous dimensional considerations previously given (Cf. in particular footnote after (13) and §3), so that for this reason, if for no other, the formula for the free energy can not be correct.

The second important point is to be found in the way in which the ionic radius (the van der Waals forces) is treated. Kramers himself emphasizes the fact that the phase integral is divergent for infinitely small ionic radius. Nevertheless he expresses the opinion that it is always possible to find a concentration at which the value of the free energy is independent of the ionic radius. This can not be admitted. Since the integral becomes infinite for $a = 0$ there can never be a concentration at which it is independent of the value of the ionic radius. As explained above, we can only hope to make the free energy independent of the particular value selected for the ionic radius if this value is contained in a range fixed from the outset. Experiment seems to indicate that this is possible in the case of aqueous solutions or other solutions of sufficiently high dielectric constant. The universal existence of a limiting law can not, however, be admitted. This statement may be illustrated by a simple estimate obtained from Gronwall, La Mer and Sandved's integration of Debye's equation. Let us consider an electrolyte in a solution of low dielectric constant (f.i. dioxane $D \sim 2$). Now Gronwall, La Mer and Sandved[12] give an expression for the activity coefficient from which the regions of concentration can easily be estimated in which the terms containing the ionic radius may be disregarded in the expression for the free energy, in comparison with the limiting term. The condition for this can be reformulated as follows:

$$1 \gg \sum_1^\infty{}_m \frac{\kappa a}{(2m-1)(2m+2)!}\left(\frac{\epsilon^2}{DkTa}\right)^{2m}. \tag{33}$$

The sum

$$\sum_1^\infty{}_m \frac{\kappa a}{(2m-1)(2m+2)!}\left(\frac{\epsilon^2}{DkTa}\right)^{2m}$$

can easily be calculated for sufficiently large

[11] It will be seen from (30) that $\Sigma(\partial W/\partial x)^2$ is proportional to κ^2 while all the terms on the left side of (27) are proportional to κ^3. L. Onsager in a lecture given before the American Chemical Society in Washington, 1933, has pointed out that the consideration of the van der Waals forces would reduce the fluctuation terms. But this could not make the right side of (27) of smaller order of magnitude (proportional to κ^4, as Fowler supposed). It follows from the general fluctuation-formula (25) that at low concentrations the fluctuation terms always become dominant as compared with the retained average values.

[12] Gronwall, La Mer and Sandved, Phys. Zeits. **29**, 376 (1928), formula 69.

values of $\epsilon^2/DkTa$. An asymptotical expression is thus obtained

$$\Sigma=\frac{1}{2}\left(\frac{DkTa}{\epsilon^2}\right)^3 e^{\epsilon^2/DkTa}. \tag{34}$$

For a reasonable value of the ionic radius

$$a\sim 5.10^8 \text{ cm}$$

there results the condition

$$\kappa\ll(1/2a)(\epsilon^2/DkTa)^3 e^{-\epsilon^2/DkTa} \tag{35}$$

or for the ionic concentration in mols p. lit.

$$c\ll 10^{-30}.$$

As will be seen, there can be no question of a valid limiting law for any reasonable concentrations. At the same time, of course, the method adopted by Gronwall, La Mer and Sandved though strictly consistent in itself is nevertheless subject to the objections, given in §3 and §4. For such low concentrations only the fluctuation term in (25) is decisive, the application of the Boltzmann theorem therefore is *even for approximation purposes*, completely illusory.

The result of these arguments can perhaps be summed up as follows: Contrary to general opinion, it is impossible by a reduction of concentration always to reach a region in which the limiting law holds. While the Debye theory as extended by Gronwall, La Mer and Sandved permits to do so, though for media of low dielectric constant only at concentrations without physical interest the consideration of the fluctuation terms excludes this possibility. There would be nothing like a limiting law in water either if the ionic dimensions happened to be, let us say, one-fiftieth of their actual value.

6. Bjerrum's Ionic Association

In the method proposed by Bjerrum for the calculation of the free energy with the aid of "ionic association" the following essential points of view stand out. Whereas Debye characterizes the interaction between a particular ion and the other ions by the introduction of the concept of an ionic cloud in which the charge is continuously distributed with variable density, Bjerrum attempts to take account of the atomistic concentration of the charge, by considering the isolated interaction between two ions. He thus subdivides the neighborhood of each ion into two parts; in a region close to the ion he determines the probability of finding another ion while outside a certain radius R Debye's method is employed. Bjerrum himself has already pointed out that this division, and the choice of the radius R contains arbitrary elements. If a pair of ions is located within the radius R, this pair is regarded as a "molecule" and is not to be considered as contributing anything to the ionic atmosphere.

This method is mathematically completely analogous to another which for decades has been used to calculate the equation of state of gases in the presence of van der Waals forces.[13] The physical justification of this procedure was given by the fact that the intramolecular forces concerned decreased with a high power of the distance. Precisely for this reason the method breaks down for Coulomb forces. Bjerrum's calculation of the ionic association also differs in two points, to its disadvantage, from the determination of the van der Walls correction: The sphere of action of two atoms within which they can be regarded as united to a "molecule," is actually indeper lent of the temperature, whereas according to Bjerrum we find it given by the expression

$$R=\epsilon_i\epsilon_k/2DkT. \tag{36}$$

The dependence on T in (36) can not be avoided since the dependence on D is quite essential and according to statistical mechanics (Cf. (2) and (3)) the excess free energy divided by kT is only a function of the expression

$$\epsilon_i\epsilon_k/DkT.$$

In Bjerrum's case this has the troublesome consequence that the Helmholtz equation, which connects energy and free energy, is no longer valid.

To prove this we refer to Bjerrum's formula for the excess free energy f of a pair of ions forming a molecule

$$e^{-(f/kT)}(4\pi R^3/3)=\int_a^R 4\pi r^2 dr e^{-(\epsilon_i\epsilon_k/DkTr)} \tag{37}$$
$$(a\ll R).$$

Differentiation of (37) with respect to T leads to

[13] Cf. R. H. Fowler, *Statistical Mechanics*, Chapter 9. See also further references.

$$e^{-(f/kT)}\frac{4\pi R^3}{3}\left(\frac{f}{kT^2}-\frac{1}{kT}\frac{\partial f}{\partial T}+\frac{3}{R}\frac{\partial R}{\partial T}\right)$$
$$=\int_a^R(4\pi r\epsilon_i\epsilon_k/DkT^2)e^{-(\epsilon_i\epsilon_k/DkTr)}dr$$
$$+4\pi R^2e^{-(\epsilon_i\epsilon_k/DkTR)}(\partial R/\partial T) \quad (38)$$

or after a slight transformation, denoting by $\bar{u}$ the average excess energy of the ion pair, to

$$f-T(\partial f/\partial T)=\bar{u}+3kT(1-e^{[f-(\epsilon_i\epsilon_k/DR)]/kT})$$
$$(\partial R/\partial T=-R/T). \quad (39)$$

The additional term

$$3kT(1-e^{[f-(\epsilon_i\epsilon_k/DR)]/kT})$$

is, in general, not small but of the same order of magnitude as $\bar{u}$.

The second point which leads to difficulties in quantitative applications is the question how the "proper-volume" of the "molecules" is to be taken into account. Ions spaced at a distance smaller than R are to be regarded as "associated." For solutions of small dielectric constant and particularly for multivalent ions, R assumes very large values, precisely on account of the long range of the Coulomb forces. Thus, for example, for univalent electrolytes in dioxane, at room temperature, R takes the value 1.4×10^{-6} cm. The volume correction in the expression for the free energy of the non-associated ions which can easily be made in the case of van der Waals forces can no longer be carried out in this instance.[14] It will also be impossible, in general, except for infinitesimally small analytic concentrations, to state to which of the other ions a particular ion belongs. The difficulty involved in the fact that the forces in electrolytes are long range forces can not be overcome by the application of a method capable of furnishing valid results for short range forces only.

To his colleague, Professor Doermann, the author wishes to express his thanks for revision of the manuscript.

[14] The argument given here will be applied in a discussion of electrical conductivity in media of small dielectric constant (Cf. Gross and Halpern, this Journal, to be published).

Dielectric Constant Studies. III. Aqueous Gelatin Solutions

A. L. FERGUSON, J. GILBERT MALONE AND L. O. CASE, *Chemistry Laboratory, University of Michigan*

(Received December 11, 1933)

Measurements have been made of the dielectric constant of gelatin solutions. A test of the Bjerrum "Zwitter-ionen" theory was furnished by a study of the effect of pH on the dielectric constant as measured by the Drude method; the data obtained support the theory. Through the application of an equation suggested by Marinesco, an attempt was made to determine the amount of water fixed by gelatin; if this equation is valid for gelatin the results obtained for absorbed water must be interpreted as indicating that the water bound by the gelatin is still free to show its dielectric properties. By means of another equation given by Marinesco relating dielectric absorption with molecular weight, values were calculated for the molecular weight of gelatin; the results obtained are consistent with those given by other methods.

BECAUSE of the probable dipole nature of proteins, it should be possible to obtain some valuable information concerning their properties through dielectric constant measurements. Thus, a test of Bjerrum's "Zwitter-ionen" theory of ampholytes might be possible. If this theory of ampholytes is correct, one would expect that gelatin, at its isoelectric point, should show a maximum dielectric constant; and the addition of either acid or base to isoelectric gelatin should cause a decrease. Again, the ultimate nature of a gel is a problem of considerable importance. What forces bind the water and maintain a solid condition even though the proportion of water is greater than 95 percent? No satisfactory answer has yet been made to this question. That the forces are electrostatic is often stated. A study of the dielectric constant of gelatin solutions under a variety of conditions offers a possible approach to this problem. If the water is bound, the dipoles are no longer free to orient and this part of the dielectric constant is decreased.

Another possible application of dielectric constant measurements to proteins is the determination of their apparent molecular weights.

A review of the investigations on gelatin shows a contradiction in the results. Thus Drude[1] and Fürth[2] found a decrease in the dielectric constant of gelatin solutions with increase in concentration. These investigators, however, did not consider the effect of pH. Marie and Marinesco,[3] on the other hand, working apparently with more care in respect to pH of the gelatin and the manner of its preparation, found a rise of the dielectric constant with increase in concentration. The contradiction in these results has not been satisfactorily explained. It may be due to the difference in the frequency employed. Drude and Fürth used a 76-centimeter wave while Marie and Marinesco used a six-meter wave. The possibility also exists that one or both sets of results do not represent true dielectric constants because of the uncertain influence of the conductivity of the solutions or other factors.

While the present work was in progress, Marinesco[4] published a comprehensive paper on the proteins. Work has been done, also, by Fricke[5] and by May and Schaffer.[6]

Apparatus and Materials

The methods used in this work are described in Papers I and II of this series.* A Drude method was used with the shorter waves and the resonance method with the longer waves. The range of wave-lengths available was from 3.5 to about 100 meters.

[1] Drude, Zeits. f. physik. Chemie **23**, 267 (1897).
[2] Fürth, Ann. d. Physik **70**, 63 (1923).
[3] Marie and Marinesco, J. chim. phys. **27**, 455–70 (1930).
[4] Marinesco, J. chim. phys. **28**, 51 (1931).
[5] Fricke, Kolloid Zeits. **56**, 166 (1931).
[6] May and Schaffer, Zeits. f. Physik **73**, 452 (1931).
* J. Chem. Phys. **1**, 836, 842 (1933).

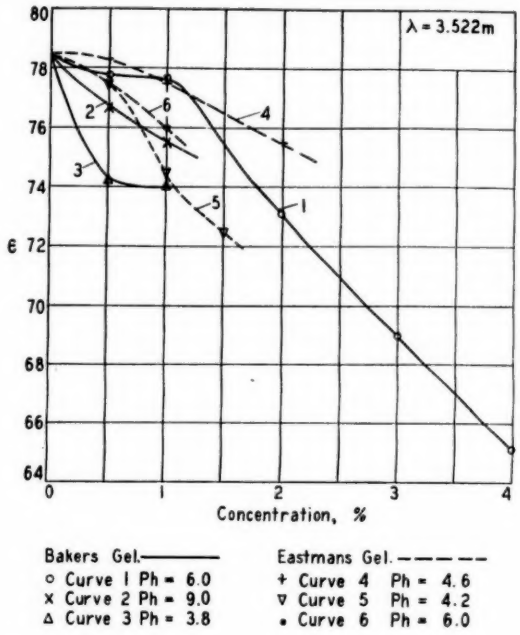


FIG. 1. Effect of concentration on the dielectric constant of gelatin solutions as measured by the Drude method at various values of pH.

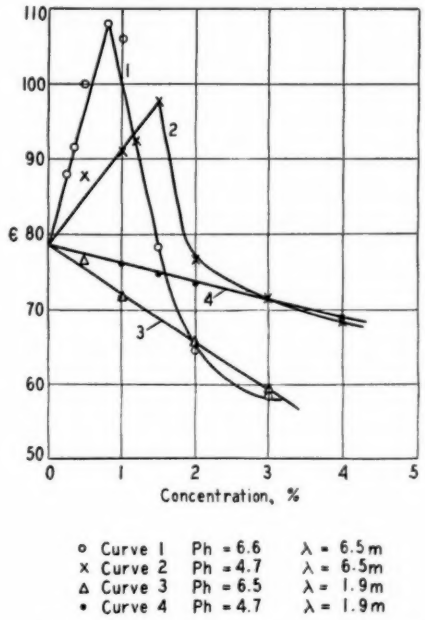


FIG. 2. Effect of concentration on the dielectric constant of gelatin solutions at different values of pH. Results of Marinesco.

The materials used were Baker's commercial gelatin and Eastman's isoelectric gelatin. Two samples of the latter were obtained, representing two different lots. The Baker gelatin contained about 1.5 percent ash, chiefly calcium salts. The Eastman product was practically ash-free. A glass electrode apparatus was used for measuring the pH. All solutions were prepared at 50°C. The pH was adjusted by adding NaOH or HCl in dilute solution to the solution of gelatin.

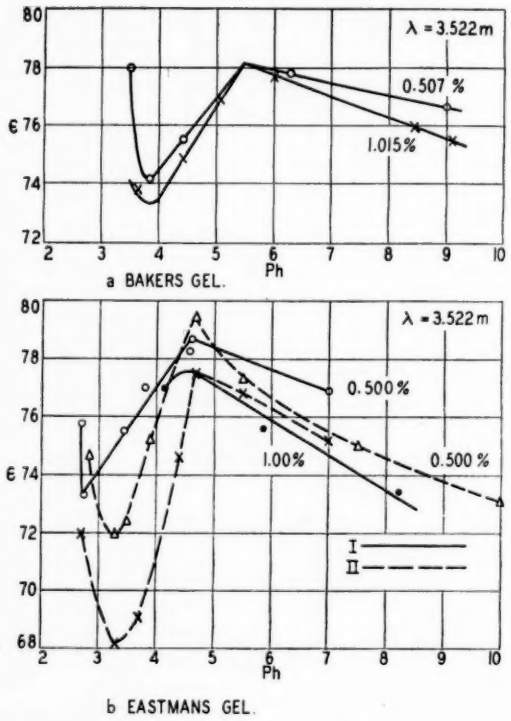
DISCUSSION OF RESULTS

A series of measurements was made at constant frequency (3.522m) with different concentrations of gelatin. The results obtained are shown by Fig. 1. The dielectric constants** are plotted as ordinates and the concentrations as abscissae. For comparison the results of Marinesco are given in Fig. 2. From these curves in Fig. 1 it may be observed that in general there is a decrease of the dielectric constant with increase in concentration of gelatin. Isoelectric gelatin, however, in the lower concentrations, gives a slight rise, as shown by curve 4.

It may be observed, also, as is shown better in Figs. 3a and b, that the dielectric constant of gelatin appears to decrease on either side of the isoelectric point; similar results were obtained by Marinesco at low wave-lengths, as may be deduced from curves 3 and 4 of our Fig. 2 of his data. These results are in agreement with Bjerrum's theory as outlined above.

At the longer wave-lengths, it is found by comparison of the values obtained by the authors (Fig. 4) with those of Marinesco (Fig. 2, curves 1 and 2) that there is no agreement. Marinesco finds a sharp rise of the dielectric constant with concentration of gelatin to a maximum which appears at a concentration of 1.5 percent in case of isoelectric gelatin, and at 0.75 percent for a gelatin of pH 6.6. After the maximum is reached, the fall with concentration is rapid until the dielectric constants measured agree with those at the lower wave-lengths.

** In place of the term, dielectric constant, the term, "square of the index of refraction," should be substituted in this case, for the values given are uncorrected for any effects of conductivity; and, in general, the n^2 term is larger than ϵ. The term, dielectric constant, will be used for convenience, however, in the whole discussion.



FIGS. 3a and b. Effect of pH on the dielectric constant of gelatin solutions as measured by the Drude method at various concentrations.

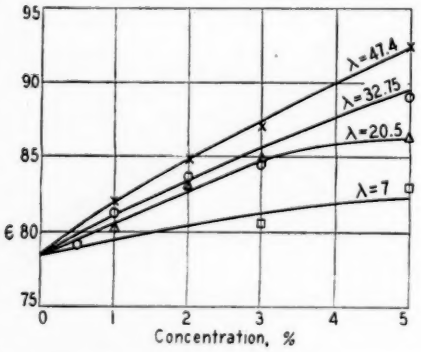


FIG. 4. Effect of concentration and of wave-length on the dielectric constant of isoelectric gelatin solutions as determined by the resonance method.

On the other hand, the values obtained by the present authors show no such sudden rises and attain no maximum within the concentration range studied, although the rate of increase of dielectric constant with concentration at the longer wave-lengths does fall off somewhat in the higher concentrations. Marinesco attributes the rise of dielectric constant to the effect of the dipoles of the gelatin molecules and the abrupt decrease to the union of dipoles to form nonpolar groups. Our results give no evidence of such a coupling; the slight flattening of the curves at the higher concentrations may properly be associated with the increased viscosity.

As previously mentioned, dielectric constant studies should give some information concerning the association of gelatin molecules with molecules of the solvent. In an aqueous gelatin solution there are presumably four factors which may contribute to the total dielectric constant. They are (1) water molecules with the dipoles free, for which $\epsilon=78.57$ at 25°C; (2) water molecules the dipoles of which are fixed, $\epsilon=2.2$; (3) gelatin molecules with dipoles not orienting in the field, $\epsilon=5.4$; (4) gelatin molecules, the dipoles of which are free. The gelatin aggregates are large and it should be possible to make the frequency so high that they cannot orient. If such were the case, the fourth factor above would disappear and the dielectric constant of the solution would be determined only by the other three.

Following Marinesco, it may be shown that if N_1, N_2 and N_3 represent the number of grams of free water, of fixed water and of dissolved gelatin in 1 cc of solution; and d_1, d_2 and d_3 represent the corresponding densities, the following relationship exists:

$$\frac{\epsilon-1}{\epsilon+2}\left(\frac{N_1}{d_1}+\frac{N_2}{d_2}+\frac{N_3}{d_3}\right)=N_1p_1+N_2p_2+N_3p_3. \quad (1)$$

Let $S=N_1+N_2=$ total g of water in 1 cc and consider $d_1=d_2$, then

$$\frac{\epsilon-1}{\epsilon+2}\left(\frac{S}{d_1}+\frac{N_3}{d_3}\right)=(S-N_2)p_1+N_2p_2+N_3p_3. \quad (2)$$

p_1, p_2 and p_3 represent the specific polarizations of free water, of electrically saturated or fixed water and of solid gelatin, respectively. Since $S/d_1+N_3/d_3=1$ (the unit of volume of the solution), then by substituting in (2) and transforming,

$$N_2=(Sp_1+N_3p_3-[(\epsilon-1)/(\epsilon+2)])/(p_1-p_2). \quad (3)$$

It should be possible by Eq. (3) to calculate the number of grams of water per cc, the dipoles of which are fixed, provided the p values are known

for fixed and free water and for gelatin with fixed dipoles.

The necessary values were obtained and the amounts of fixed water were calculated from our own data at 3.522 meters, as well as from Marinesco's data at 1.9 meters. These values are recorded in Table I. The first column gives the

TABLE I. *Fixation of water molecules by gelatin.*

pH	Spec. vol. gelatin	p_3	N_3	S	ϵ of solution	$\frac{\epsilon-1}{\epsilon+2}$	H
6.6	.724	.4488	.005	.9964	76.4	.9617	.131
6.6	.724	.4488	.01	.993	71.8	.9593	.270
6.6	.724	.4488	.02	.9855	65.6	.9554	.110
			Baker's gelatin measurements by authors				
6.6	.790	.491	.01015	.9920	77.1	.9621	−.2665
6.6	.790	.491	.00507	.9961	77.9	.9621	−.1745
6.6	.790	.491	.0203	.9842	76.3	.9617	−.289
3.8	.790	.491	.00507	.9961	74.5	.9608	.296
3.8	.790	.491	.01015	.9920	73.0	.9600	.0443
			Eastman's gelatin measurements by authors				
6.6	.790	.491	.01015	.9920	75.2	.9602	−.1328
8.2	.790	.491	.01015	.9920	73.5	.9617	.0147
3.8	.790	.491	.00446	.9965	76.3	.9617	.0663
2.76	.790	.491	.00446	.9965	73.3	.9602	.553

$p_1 = 0.9630$
$p_1 - p_2 = 0.6765$

pH of the solutions; the second, the specific volume of solid gelatin; the third, p_3, or the specific polarization of solid gelatin; the fourth, the concentration of gelatin in grams per cc; the fifth, S, the total grams of water per cc; the sixth, ϵ, the dielectric constant of the solution. The last column, H, contains the calculated values for the grams of water fixed per gram of gelatin, which may be simply calculated from N_2 of Eq. (3). In the use of this formula p_3 was calculated by using Fürth's value of 5.9 for the dielectric constant of solid gelatin.

It is clear from our results, which give, in some cases, negative values for H, that this method cannot be used to determine the extent to which water is bound by gelatin. Although it is possible that the frequency used was not high enough completely to prevent the rotation of the gelatin molecules, a more likely interpretation of the results is that the water bound by the gelatin is still partially free to show its dielectric properties.

The determination of molecular weights by means of dielectric constant measurements is based upon the equation given by Marinesco in the form

$$M = \tfrac{1}{3}(\lambda/C)(RT/\eta V),$$

where

M = molecular weight
T = temperature; here 298°K
η = viscosity of solvent; here 0.011 poises
λ = wave-length in region of dispersion
R = gas constant; 83.2×10^6 ergs/degree
V = specific volume of the material in solution; here 1.38 cc/gm
c = velocity of light, 3×10^{10} cm/sec.

Since dispersion was found from 7 meters to 50 meters, the molecular weights indicated range from 13,500 to 96,300. Gelatin appears, therefore, to possess molecules of different molecular weights. Although this method is yet unproved, the values obtained are reasonable at least. The use of the ordinary viscosity as the effective viscosity acting on the molecules is of course open to question.

It is noteworthy that the dielectric constant of a gelatin solution is unaffected by the setting of the solution to give a solid. Solutions show a higher dielectric constant when first prepared and this gradually decreases, but the rate is not influenced by the setting, at least so far as may be observed. When a solution has visibly set, the dielectric constant continues to fall for some hours thereafter, although with a decreasing rate.

These observations, while in agreement with those of Fricke,[5] are not in agreement with those of Marinesco.[4] Marinesco assumes that the maximum of the dielectric constant-concen tration curve (Fig. 2, curve 1) determined at 6.5 meters wave-length has a unique significance He attributes the rapid rise in dielectric constant of the solution to the dipole nature of the molecules of added gelatin. At the concentration 0.75 percent, which is for the apex of the curve, he assumes the dipoles to combine and thus produce a rapid decrease in dielectric constant of the solution with increase in concentration. He further states in the case of solutions of pH 6.6 that the apex of the curve represents the concentration at which gel formation is first possible. This explanation is not satisfactory because the same reasoning cannot be applied to isoelectric gelatin, since the maximum in this case is at about 1.5 percent concentration, while

it is well known that isoelectric gelatin will set before that concentration is reached and also that gelatin sets most readily at the isoelectric point and not least readily, as Marinesco's interpretation would lead us to believe.

The picture of the nature of gelatin solutions that may be drawn from our data is approximately the conventional one. The gelatin molecules or particles in suspension are of graded size and of rather large molecular weights, ranging at least from about 5000 to 100,000. The gradation in size of molecule is apparently a continuous one, although gradations in steps of the order 10,000 are not excluded by the accuracy of the data obtained. This method does not exclude the possibility of other molecules or aggregates being present so long as they have no dipole moment. This situation is not likely in the case of proteins because of the large moments consistently obtained for the amino acids which are their decomposition products. It appears, also, that no coupling of the dipoles occurs and that gel formation is unaccompanied by any marked change in the dielectric properties.

Dielectric Constant Studies. IV. The Moments of Some Inorganic Compounds

MARY G. MALONE* AND A. L. FERGUSON, *Chemical Laboratory, University of Michigan*

(Received December 11, 1933)

The moments of some inorganic compounds have been determined, some in more than one solvent and the best values are believed to be: for $SbCl_3$, 3.12; $SbBr_3$, 2.47; SbI_3, 1.58; AsI_3, 0.96; $AsBr_3$, 1.60; PI_3, 0.0; AsF_3, 2.65; and $LiClO_4$, 7.84 Debye. The dielectric constant of solid AsF_3 was measured and found to be 5.7. The moments of the molecules measured have been calculated from the electronegativity of the elements and compared with the measured values. A fair agreement is found with deviations greatest for molecules of highest polarizability and possessing large moments. The electronegativity values were deduced from the measurements of the hydrogen compounds or from their periodic relationship.

THE intimate relationship existing between the properties of a molecule and the electrical symmetry or electric moment has led to the belief that the latter gives considerable information concerning the nature and extent of the forces uniting atoms. Indeed so general has this belief become that the terms polar and nonpolar have often been confused with ionic and covalent. Atomic combinations between like atoms are generally known to be nonpolar and it is also generally accepted that true ionic bonds like those of the alkaline metal halides are strongly polar. A growing tendency may be noted to consider that there is no sharp division between bonds of the ionic and covalent type but, rather, that there is a general transition from one type to the other.

It has been pointed out previously[1] that probably all covalent bonds are nonpolar and that the electric moment may be considered a measure of the deviation of the bonds from the covalent type. The measured values of the moments of simple molecules were so limited that the present study was undertaken in order to extend our knowledge in this direction and thus provide for a more adequate generalization in this field.

PREPARATION OF MATERIALS AND SOLUTIONS

Benzene

The thiophene-free material was stirred with sulphuric acid until it was no longer colored, washed with water and sodium hydroxide solution and stirred with water for some time. The benzene was then dried with calcium chloride and fractionated. The middle portion was fractionally frozen, redistilled from phosphorous pentoxide and dried over sodium.

Carbon disulfide

The c.p. quality was further purified by shaking with mercury until the mercury was no longer tarnished, fractionated, dried by refluxing with phosphorous pentoxide, again fractionated and redistilled just before using. No difference in capacity was noted in the different samples prepared if they were measured just after distilling. After standing for some time, however, a slight change was detected.

Dioxane

Eastman's best quality was further purified by refluxing with sodium, fractionally distilling and standing over sodium. Different samples of dioxane showed different dielectric constants depending upon the length of time it was allowed to stand over freshly cut sodium. Constants for dioxane were redetermined every day it was used.

* Rewritten from a thesis by Mary G. Malone in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Michigan.

[1] J. G. Malone, J. Chem. Phys. **1**, 197 (1933).

Carbon tetrachloride

Eastman's best quality was fractionally distilled, dried over calcium chloride and redistilled.

Antimony trichloride

Baker's c.p. grade was purified by fractional distillation under reduced pressure. The distillate was collected in the same vessel in which the solution was prepared so that no moisture was admitted. Benzene solutions so prepared showed no cloudiness.

Antimony tribromide

Coleman and Bell c.p. quality was purified in the same manner as the trichloride. The capacity of the carbon disulfide solutions changed with time, a noticeable change occurring in half an hour. To avoid this the solutions were made at 25° and measurements taken immediately and at short intervals over a period of several minutes. The values obtained in this way did not change during the intervals.

Antimony triiodide

The Eimer and Amend c.p. quality was recrystallized from carbon disulfide. The crystals were light in weight, bright red in color and every face shone with a luster. They did not tarnish when exposed to air for a short time. The carbon disulfide solution of antimony triiodide was clear and yellow in color and did not darken with time. The capacity measurements did not change with time.

Arsenic tribromide

The Eimer and Amend c.p. quality was purified by fractional distillation and collected in the manner described for the antimony chloride. The capacity measurements did not change with time.

Arsenic triiodide

The Coleman and Bell c.p. quality was purified by recrystallization from carbon disulfide. The crystals were red, shiny plates. They were dried from the carbon disulfide by dried carbon dioxide gas and handled in carbon dioxide during use. They were attacked by air, losing their luster. They formed an orange-to-red solution in carbon disulfide in contrast to the yellow one produced by the antimony compound. The solution turned dark after several days. No change of capacity with time was noted during the time the solution was in the cell.

Phosphorus triiodide

It was prepared by refluxing, for some time, equivalent quantities of phosphorus and iodine dissolved in carbon disulfide. After the reaction was complete the solution was concentrated, cooled, and the red crystals were deposited. They were washed and recrystallized twice. The phosphorus triiodide fumed in the air and had to be handled in a dried carbon dioxide atmosphere. The carbon disulfide solutions were yellow in color and showed no tendency to darken when kept sealed from the air for three weeks. The capacity measurements were constant.

Arsenic trifluoride

It was prepared in a three-compartment dry glass apparatus which was evacuated. Equivalent weights of calcium fluoride and arsenious oxide were placed in the first compartment and a large excess of concentrated sulfuric acid added from a dropping funnel. The arsenic trifluoride formed was distilled into the second compartment, the third compartment being closed from it by a stopcock. The second compartment was closed from the first and the material kept until time for use. At that time a small first portion was distilled into the third compartment. It was removed by a vacuum pump and the middle portion distilled into this compartment for use. Solutions were made by adding the liquid from this compartment directly into the benzene in a dry nitrogen atmosphere. The glass apparatus and cell were only very slightly etched after use and the density bottle to a slightly greater extent. Some AsF_3 was kept in good condition in the glass apparatus for several months.

Lithium perchlorate

A very pure sample was obtained from Professor H. H. Willard. It was dried by fusing.

Iodine monochloride

Eimer and Amend c.p. quality was purified by a fractional recrystallization.

Experimental

A heterodyne apparatus similar to that employed by other workers[2] in this field was used for the solution measurements. For the solid arsenic trifluoride and iodine monochloride, a resonance apparatus was used, described in a previous paper[3] from this laboratory.

Two cells were used for the solution measurements, each consisting of five coaxial gold-plated brass cylinders. The plates of one of the cells were spaced with mica and those of the other with Bakelite. Leads were made to mercury cups. Different capacities could be obtained by using different combinations of the plates. The cells had maximum capacities of about 193 and 183 mmf, respectively. Small cells with platinum plates were used with the resonance apparatus.

The density bottle was similar to that described by Dr. Wooley.[4] The 33 cc bottle had a 2 cc graduated pipette attached making it possible to take readings at different temperatures with one weighing. An error of 0.03 percent could occur due to the volume reading.

The apparatus was tested by measuring the moment of antimony trichloride in benzene. A value of 3.84 was obtained, which is in good agreement with the values 3.6 by Werner,[5] 4.11 by Bergman and Engel[6] and 3.75 to 3.95 by Smith.[7]

In the Tables I to XI inclusive, c_2 represents

Table I. *Moment of $SbCl_3$ in carbon disulfide at 25°.*

$P_{200}' = 205$ $\mu = 3.12 \pm 0.05$

c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	1.2600	2.634				
0.00243	1.2659	2.692	21.85	238	44	194
0.00451	1.2685	2.731	22.20	217		173
0.00707	1.2718	2.789	22.62	205		161
0.00839	1.2763	2.806	22.77	194		150
0.01281	1.2834	2.913	23.28	181		137
0.01689	1.2930	2.996	24.14	187		143

Table II. *Moment of $SbBr_3$ in benzene at 25°.*

$P_{200}' = 225$ $\mu = 3.28 \pm 0.1$

c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	0.8374	2.276				
0.00404	0.8858	2.351	27.60	273	50	223
0.00512	0.8899	2.369	27.82	267		217
0.00514	0.8900	2.363	27.79	263		213
0.00712	0.8949	2.406	28.40	274		224
0.01270	0.9121	2.495	29.70	269		219

Table III. *Moment of $SbBr_3$ in carbon disulfide at 25°.*

$P_{200}' = 225$ $\mu = 2.47 \pm 0.1$

c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	1.2600	2.634				
0.002333	1.2691	2.674	21.69	180	50	130
0.003638	1.2745	2.692	21.85	170		120
0.003959	1.2748	2.700	21.92	173		123
0.007421	1.2888	2.757	22.45	172		122
0.013659	1.3120	2.844	23.23	161		111

Table IV. *Moment of SbI_3 in carbon disulfide.*

$P_{200}' = 52.5$ $\mu = 1.58 \pm 0.1$

c_2	T	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	25°	1.2600	2.633				
0.001603		1.2706	2.652	21.465	124.8	76.8	48.0
0.001945		1.2731	2.658	21.52	132.9		53.1
0.002140		1.2753	2.660	21.515	124.5		47.7
0.002643		1.2797	2.665	21.56	117.1		40.3
0.000	36°	1.2501	2.610				
0.003944		1.2778	2.662	21.70	129.3		52.5

Table V. *Moment of $AsBr_3$ in carbon disulfide at 25°.*

$P_{200}' = 54.0$ $\mu = 1.60 \pm 0.05$

c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	1.2600	2.634				
0.002648	1.2685	2.651	21.478	88.0	37.6	51.4
0.005719	1.2793	2.671	21.67	85.7		48.1
0.008448	1.2887	2.689	21.84	85.2		47.6
0.009160	1.2910	2.697	21.91	86.1		48.5
0.010454	1.2960	2.707	21.90	78.4		40.8
0.011953	1.3005	2.713	22.07	85.3		47.7

Table VI. *Moment of AsI_3 in carbon disulfide at 25°.*

$P_{200}' = 19.0$ $\mu = 0.96 \pm 0.1$

c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	1.2600	2.634				
0.000931	1.2647	2.636	21.329	73.5	59	14.5
0.002160	1.2734	2.648	21.42	78.7		19.7
0.002715	1.2760	2.649	21.46	77.4		18.4
0.004226	1.2831	2.657	21.55	80.5		21.5
0.007914	1.3027	2.679	21.71	74.0		15.0

[2] Smyth, *Dielectric Constant and Molecular Structure*, p. 54, Chemical Catalogue Company, New York, 1931.

[3] J. G. Malone, A. L. Ferguson and L. O. Case, J. Chem. Phys. **1**, 836 (1933).

[4] Wooley, J. Am. Chem. Soc. **55**, 3518 (1933).

[5] Werner, Zeits. f. Anorg. allgem. Chemie **181**, 154 (1930).

[6] Bergman and Engel, Zeits. f. physik. Chemie **B13**, 232 (1931).

[7] Smith, Proc. Roy. Soc. (London) **A136**, 256 (1932).

TABLE VII. *Moment of PI_3 in carbon disulfide at 25°.*

$\mu=0$

c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	1.2600	2.633				
0.001650	1.2682	2.636	21.334	43.83	49.75	0
0.002708	1.2730	2.639	21.380	51.69		
0.004840	1.2832	2.641	21.42	47.52		
0.005079	1.2847	2.644	11.445	51.12		
0.007206	1.2925	2.648	21.51	51.34		

TABLE VIII. *Moment of AsF_3 in benzene at 25°.*

$P_{2\infty}'=145.6$ $\mu=2.65\pm0.05$

c_2	d	ϵ	P_{12}	P_2	P_{E+A}	P_2'
0.000	0.8734	2.276				
0.01499	0.8869	2.434	28.71	164.1	26.8	137.3
0.02371	0.8948	2.521	29.78	162.5		135.7
0.02914	0.8997	2.574	30.43	156.5		129.7
0.03535	0.9052	2.641	31.21	155.6		128.8

TABLE IX. *Moment of $LiClO_4$ in dioxane at 25°.*

$P_{2\infty}'=1285$ $\mu=7.84\pm0.05$

c_2	d	ϵ	P_{12}	P_2	P_E	P_2'
0.000	1.0310	2.315				
0.002767	1.0345	2.544	28.92	1048	24	1024
0.003970	1.0362	2.620	29.92	990		966
0.004445	1.0370	2.672	30.40	994		970
0.000	1.0310	2.325				
0.0005967	1.0318	2.381	26.88	1258		1234
0.001263	1.0326	2.435	27.60	1172		1148
0.002004	1.0336	2.498	28.37	1133		1109
0.002402	1.0342	2.524	28.68	1106		1082

the mole fraction of the polar substance, ϵ the dielectric constant of the solution, d the density, P_{12} the polarization of the mixture and P_2 the polarization of one solute. P_2 is calculated from the following relationship,

$$P_{12}=[(\epsilon-1)/(\epsilon+2)]\cdot(c_1M_1+c_2M_2)/d$$

and

$$P_2=(P_{12}-P_1c_1)/c_2$$

where c_1 and c_2, M_1 and M_2, and P_1 and P_2 are mole fractions, molecular weights and polarizations of the components.

The P_{E+A} values were obtained from the dielectric constants of the solid polar material obtained in case of $SbCl_3$, $SbBr_3$, $AsBr_3$, AsI_3 and PI_3 from measurements by Schlundt.[8] The dielectric constant of solid AsF_3 was measured by the use of the resonance apparatus and found to be 5.7. The P_E value of $LiClO_4$ was obtained from refractive index measurements. An Abbé refractometer was used; therefore this value represents the order of magnitude and not an exact measurement. For use in calculating the P_{E+A} values the density of the solid material was obtained from the literature in all cases except PI_3 and AsF_3, which had to be measured. The density of PI_3 was found to be 3.89 at 25° and that of AsF_3, 3.01 at the same temperature as the dielectric constant was measured.

The P_2' value represents P_2-P_{E+A}. The values P_2' were obtained by extrapolating the $P_2'-c_2$ curves to infinite dilution. The moment was obtained from the relation

$$\mu=0.0127(P_{2\infty}'T)^{\frac{1}{2}} \text{ Debye.}$$

An attempt is made to give an evaluation of the size of the known errors in giving the size of the moment. However, this is only an approximation but given so that other authors may not make use of these values to a greater accuracy than the values justify.

An attempt was made to measure the moment of $HgCl_2$ in benzene. Its insolubility made accurate measurements impossible, but the values indicated a zero moment, although a small moment would not be excluded.

Considerable work was done in an attempt to measure ICl in CCl_4 solution. Just what percent of dissociation one has in such a case is not known. The red solution tarnished the gold plate of the cell during the set of measurements. The solution was kept in an inert atmosphere during use. The temperature and dielectric constant curve of solid ICl was studied by means of the resonance apparatus. A change of dielectric constant with temperature was marked, as is shown in Table X. The reason for such changes is

TABLE X. *The change of dielectric constant of solid ICl with temperature.*

Temp.	ϵ	Temp.	ϵ	Temp.	ϵ
−48°	7.0	−28°	9.4	−15°	11.3
−40°	7.4	−25°	9.5	−12°	12.9
−37°	8.0	−20°	10.4	−11°	13.7
−34°	8.3	−18°	10.8		

[8] Schlundt, J. Phys. Chem. **5**, 503 (1901); **8**, 122 (1904); **15**, 381 (1911).

not apparent. Somewhat similar changes in the dielectric constant of the hydrogen halides have been ascribed to the effect of rotational energy.*

TABLE XI. *Polarization of ICl in CCl_4 at 25°.*

$P_{2\infty}' = 60$

c_2	ϵ	d	P_{12}	P_2
0.000	2.230	1.5837		
0.003423	2.239	1.5863	28.35	58.4
0.005060	2.243	1.5880	28.38	55.9
0.005126	2.244	1.5886	28.39	55.5
0.006238	2.2465	1.5891	28.43	55.1
0.008589	2.251	1.5912	28.47	54.7

Strong electrolytic types of atoms are usually considered to possess high moments. The measurements given here for lithium perchlorate further substantiate this view. It may be that it is even a better case than the silver perchlorate measurement[9] so often quoted, for Gosh[10] was unable to show complex formation between perchlorates and dioxane.

The theoretical treatment follows that of the work of Malone[1] previously referred to. The electronegativity scale has been extended on the basis of the periodic table, as is recorded in Table XII. The bonds not in parenthesis are

TABLE XII. *Electronegativity of non-metallic elements referred to H as zero.*

	0.28	0.40	
	N	O	F
	1.04	1.32	(1.72)
0.69			
	P	S	Cl
	0.36	0.63	1.03
0.26			
	As	Se	Br
	0.10	(0.37)	0.78
0.40			
	Sb	Te	I
	(−0.30)	(−0.03)	0.38

those taken from the experimental data on the hydrogen compounds. The bonds in parenthesis were obtained by the addition or subtraction of the differences in either the horizontal or vertical columns. For example, the value of F was obtained by adding 0.69, the difference between N and P and between O and S, to the value of Cl to obtain 1.72 for F.

In order to use such a table to calculate moments it must be assumed that electronegativity is an additive property. Also, in the case of several vector moments present in a molecule, the angles present must be known. The reaction of one moment on another is a matter of some importance but its effect is difficult to evaluate. One assumes also that the angles remain constant as long as only two species of atoms are concerned.

It is to be expected in highly polarizable atoms with high moments that considerable discrepancies would be encountered. But it may be assumed that the agreement will be the best in those cases where the conditions most nearly approximate the polarizability conditions prevalent in the hydrides, upon which the table is based. This has proved to be the case and is to be observed, especially in the case of the arsenic fluoride. The agreement of the calculated and the observed value is very good. This value is one of great interest. All modifications of the scale given here indicate that fluorine is an element of greater electronegativity than any other. On this basis, the moment of HF should be greater than the moment of HCl. For the same reason the moment of AsF_3 should be greater than the moment of $AsCl_3$, as was found to be the case. Some recent work by Kirkwood[11] has indicated a moment of about 0.8 for HF. Our results require a much higher value. A measurement of the moment of gaseous HF would be very valuable and is contemplated in this laboratory.

Since complexes of benzene and antimony chloride and bromide are formed[12] it is of interest to have values for the moments of these materials in another solvent. Carbon disulfide was selected for the purpose, since there is no evidence available to indicate that complexes are formed with it. The measurements showed only slightly lower moments in each case. These lower values are listed in Table XIII.

The antimony triiodide was measured only in carbon disulfide where its solubility is somewhat

* Professor Barker informs us that this is impossible in this case

[9] Williams, Phys. Zeits. **29**, 174 (1928).

[10] Gosh, J. Chem. Soc. **107**, 159 (1915).

[11] Kirkwood, Phys. Zeits. **33**, 259 (1932).

[12] Smith and Davis, J. Am. Chem. Soc. **41**, 411 (1922); Cremer and Duncan, J. Chem. Soc. 2750 (1930).

TABLE XIII. *Calculated and observed moments.*

Mol.	Calc.	Obs.	Refr.	Mol.	Calc.	Obs.
SCl_2	0.51	0.56	Smith	$SbCl_3$	2.23	3.12*
PF_3	2.01			$SbBr_3$	1.81	2.47*
PCl_3	0.98	0.8	Berg.	SbI_3	1.14	1.58*
		0.9	Smith			
PBr_3	0.62	0.61	Berg.	SbH_3	0.50	
PI_3	0.0	0.0*		SbF_3	3.41	
$AsCl_3$	1.44	1.97	Berg.	NCl_3	0.0	
		2.15	Smith			
$AsBr_3$	1.05	1.66	Berg.	NBr_3	0.36	
		1.60*				
AsI_3	0.43	0.96*		NI_3	0.92	
AsF_3	2.53	2.65*		NF_3	0.97	
IBr	0.40			ICl	0.65	0.9–1.1*

* Work in this laboratory.

Smith, Proc. Roy. Soc. **A138**, 154 (1932); **136**, 256 (1932); Bergman and Engel, Zeits. f. physik. Chemie **B13**, 232 (1931).

greater than in benzene. The value found, 1.58, leads us to believe the value 0.40 ascribed to Williams by Werner[13] is too low.

The measured moments of the three antimony compounds vary considerably from the calculated ones. It must be borne in mind, however, that these were calculated from the predictions in the periodic table and not on a measured hydride, as was true in the other cases. As was previously mentioned, molecules of high polarizability with high moments should be expected to deviate somewhat from the calculated values and it is borne out in these cases. In predicting a moment for SbF_3 from these data one would place it nearer the calculated value than the other antimony compounds. Its insolubility in nonpolar solvents so far available prohibited a measurement.

Arsenic tribromide was measured in carbon disulfide in order to compare it with the measurements by Bergman and Engel[14] in CCl_4. It is assumed that carbon tetrachloride and carbon disulfide are compounds of similar polarity. The agreement is all that could be desired.

In the case of PI_3 one would expect only a very small moment, as the moment of the bond P–I is negligible. This has been found to be the case, the measured moment could not be distinguished from zero.

Any moment calculated from the data given for ICl (if one is justified in making such a calculation) is much higher than the one expected from the bond moments. ICl is another highly polarizable molecule with a reasonably high moment.

CONCLUSION

The evidence presented by the additional measured values of the dipole moments of inorganic compounds indicates the advantages and the limitations of attempting to treat the concept of moments on the basis of electronegativity. It is already indicated that the concepts which this method introduces are not wholly adequate to give quantitatively the moments in some cases. The method on the other hand has the merit of allowing generally recognized but poorly stated concepts to be expressed in terms that are capable of quantitative evaluation. A great mass of dipole moment data has been accumulated, chiefly on complex organic molecules, which if properly interpreted would, no doubt, be of great value. Such interpretations must be based on the fundamental relation of dipole moment to other properties of the molecule and these in the opinion of the authors can only be obtained by adequate study of the simpler cases.

The authors gratefully acknowledge the assistance and interest of Dr. J. G. Malone.

[13] Williams and Werner, Zeits. f. anorg. allgem. Chemie **181**, 154 (1930).

[14] Bergman and Engel, Zeits. f. physik. Chemie **B13**, 232 (1931).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Diffusion of Hydrogen Through Metals: Fractionating the Hydrogen Isotopes

In the summer of 1930 a striking example of the diffusion of hydrogen through metals was observed. The diffusion of the hydrogen took place under the following conditions. Two pieces of steel sheet metal, each about 1/32" (0.75 mm) thick, were welded together carefully at the four edges and immersed as cathode in an acid solution (mixture of sulfuric and hydrochloric acids). The temperature of the acid bath was about 70°C. The current density employed was about 22 amperes per dm². At the end of two hours a very marked bulging of these sealed plates or iron "pillow" was observed. Thereupon the seal was broken and the gas collected over water and tested. The clear, sharp explosion that was obtained showed the presence of hydrogen. This experiment was repeated several times and always the same results were obtained. We decided to determine whether or not the hydrogen thus collected within the metal "pillow" was substantially the lighter of the two hydrogen isotopes.

Preliminary qualitative experiments were carried out with tubes of iron, nickel and palladium. The walls of the iron tubes were about 0.8 mm thick, those of the nickel 0.2 mm and 0.4 mm respectively, and those of the palladium about 0.25 mm. The baths used were: a 25 percent (by volume) sulfuric acid solution, a 10 percent NaOH solution (by weight), and a 25 percent $MgSO_4 \cdot 7H_2O$ solution (by weight). The temperature varied from 85 to 90°C. The current density employed varied from a little less than 11 amperes per dm² to over 120 amperes per dm². The anode used was platinum. The gas passing through the walls of the tubes was collected over water. The palladium tube gave the best performance. A 25 percent sulfuric acid solution was used and the gas gave a clear test for hydrogen.

An apparatus was then set up whereby the hydrogen passing through the palladium tube wall could be "burned" and the resulting water collected. The electrolyte consisted of special water containing about ½ percent "heavy water," to which was added fuming sulfuric acid, in the proportion 335 cc special water, to 25 cc fuming sulfuric acid. During the electrolysis the volume of the solution was kept constant. The temperature was maintained at about 85°C. A current density of 60 amperes per dm² was employed. The voltage drop was 4.3 volts. A platinum anode was used. The length of the palladium tube immersed in the electrolyte was 25 cm. At the end of 28 hours, about 2 cc of water had collected. Its specific gravity was found to be 1.00020. This would indicate that neither light nor heavy hydrogen *alone* passed through the walls of the palladium tube, but a mixture of both.

An experiment was then arranged to determine the rate at which hydrogen passed through the walls of the palladium tube used in the preceding experiment. The tube was carefully cleaned. A new solution was used consisting of distilled water 75 percent by volume; c.p. sulfuric acid 25 percent by volume. The temperature of about 70°C was maintained for each run. The experiment was continuous, that is, with change of current density the apparatus and solution were left undisturbed. The volumes of gas were collected under as similar conditions as possible. The temperature of the water, over which the gas was collected, was 20.5°C. The barometric pressure was 766.4 mm. The data are given in Table I.

TABLE I.

Current density amp./dm²	Voltage	Volume gas collected cc	Time min.	Volume gas per minute cc
100.	7.5	1000	48	20.8
50.	5.2	430	120	3.5
20.	3.2	60	60	1.0

Another experiment was run to determine whether oxygen would diffuse through the walls of this same palladium tube. The same electrolyte was used as in the preceding experiment. A temperature of 40°C was maintained. A current density of 100 amp. per dm² was used. The cathode was platinum. No gas was observed to come through the tube even after 2½ hours. During the run, however, a dark violet-colored film was observed on the

surface of the tube. That film might have acted to prevent the diffusion of the oxygen through the walls of the tube.

These preliminary experiments show that with the palladium cathode fractionation of the two isotopes does occur, protium, the lighter isotope, diffusing through more readily. The experiments with the iron "pillow" indicated that we are dealing with extraordinary high pressures. On the basis of the overvoltages involved, a simple calculation indicates that these pressures or the fugacities are of the order of a million atmospheres.

COLIN G. FINK,
HAROLD C. UREY,
D. B. LAKE

Columbia University,
New York, New York,
January 3, 1934.

Isotopic Fractionation of Hydrogen

Water containing approximately one part deuterium to 200 parts of protium was electrolyzed with a current of one ampere and the hydrogen produced was passed over copper oxide at a temperature of 200°C. The rate of flow of the hydrogen was such that roughly 50 percent of it was converted into water and the remainder was forced over copper oxide at about 600°C, so that at the high temperature all the hydrogen reacted to form water. The two fractions of water, 10 ml each, were condensed separately, and distilled into pycnometers calibrated at 25°C. The sample of water formed at 200°C had a mass of 6.6 mg less than the 10 ml formed by the complete combustion.

The experiment was repeated using two cells in series so that the rate of flow of hydrogen was twice as great and the surface of copper oxide was kept the same. (80 g of copper gauze, number 26 wire, was used in each reaction chamber.) This time the light fraction of 10 ml weighed 5.0 mg less than the heavy fraction. The samples of water were interchanged in the pycnometers and identical mass differences were found.

HERSCHEL HUNT

Purdue University,
West Lafayette, Indiana,
January 11, 1934.

Unimolecular Decomposition at High Pressures[1]

A recent letter by Coffin and Geddes[2] states that the first order coefficient for the decomposition of paraldehyde decreases by 50 percent when the pressure is increased from a few mm to 18 atm. They suggest as an explanation that the reactive degrees of freedom lie in the center of the molecule and are not excited directly by collisions; it is supposed that the probability of reaction per unit time will therefore increase when an activated molecule is undisturbed. In considering this mechanism it will be helpful to adopt the usual convention that the actual reaction may be mentally suppressed without otherwise changing the behavior of the molecule. States for which some small group of internal vibrations has at least a critical energy decompose spontaneously when the convention is relaxed; while it is maintained, they are present at the Maxwell-Boltzmann quota. Coffin and Geddes make the plausible-sounding assertion that the rate at which these states are produced is less at high pressures; to maintain the same equilibrium, however, it would be necessary for the rate at which such states are destroyed to decrease to the same extent. It seems impossible to believe that the occurrence of collisions could prevent the central degrees of freedom from losing energy. A closer understanding of the fallacy is perhaps obtained by means of the following simple model; the molecule has three degrees of freedom, A, B and C; only A is directly affected by collisions, and A is connected with C only through the intermediary B; the probability that a quantum of energy will be transferred from A to B, B to A, B to C or C to B is k sec.$^{-1}$. It is then readily shown that if A is given a quantum when B and C have none, the chance that C has the quantum at the expiration of time t increases initially as $(kt)^2/2$, and it would seem that such a model gives the Coffin-Geddes effect. This is not so, however; the collision will have no influence unless the quantum is at A, since only A participates in collisions; if the quantum is at A, the deactivation which occurs is perfectly balanced by activation of A in some other molecule. In general, it will be true that if collisions cannot directly excite some special vibration, they cannot directly quench it either.

LOUIS S. KASSEL[3]

U. S. Bureau of Mines,
Pittsburgh Experiment Station,
Pittsburgh, Pennsylvania,
January 12, 1934.

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] C. C. Coffin and A. L. Geddes, J. Chem. Phys. 2, 47 (1934).

[3] Associate physical chemist.

Thermal Decomposition of Deuterium Iodide

We have previously pointed out[1] that the thermal dissociation of hydrogen iodide should be dependent on the concentration of deuterium in the hydrogen iodide. Experiments in this laboratory have verified these theoretical calculations.

Hydrogen iodide was prepared from its elements and purified by three vacuum distillations. The reaction vessel

[1] H. C. Urey and D. Rittenberg, J. Chem. Phys. 1, 137 (1933).

was filled to about 60 cm pressure and sealed off. The reaction vessel was kept at the chosen temperature for a period about 15 times longer than would be necessary for ordinary hydrogen iodide to attain equilibrium. The reaction vessel was then pumped out through a break seal and the iodine and hydrogen iodide frozen out in traps with liquid air. The iodine and hydrogen iodide were dissolved in water and the solution analyzed for I_2 and H^+. At no time were the gases in contact with anything but glass. The fraction decomposed, h, was calculated from the equation

$$h=2[I_2]/(2[I_2]+[HI]),$$

where $[I_2]$ is the moles of I_2 at equilibrium, and $[HI]$ the moles of HI at equilibrium. The results are given in Table I. h_B is the value Bodenstein[2] gives for ordinary hydrogen iodide. Δh is the difference in the fraction decomposed of the sample rich in deuterium iodide and pure protium iodide.

The concentrations of the 13.5 and 40.0 percent samples were determined by W. Bleakney on his mass-spectrograph.[3]

TABLE I.

Conc. H^2	h exp.	h calc.	Δh exp.	Δh calc.
	$T=398°C$		$h_B=0.20703$	
0.0%	0.20719	—	—	—
13.5	0.20838	0.20878	0.00119	0.00175
	$T=468°C$		$h_B=0.22772$	
0.0	0.22724	—	—	—
40.0	0.23287	0.23326	0.00563	0.00602
72.1	0.23877	0.23904	0.01153	0.01180

The concentration of the 72.1 percent sample was determined by burning 500 cc of hydrogen iodide and determining the concentration of deuterium in the resultant water by the interferometric method which will be published shortly by Crist, Murphy and Urey. They assume that the molecular volume of deuterium oxide is the same as protium oxide. However, if the mol volume is that claimed by G. N. Lewis, the concentration of the sample will be about 76.5 percent. A change of 1 percent in the concentration of the deuterium will change Δh by 0.00013. This uncertainty will, however, not apply to the 13.5 and 40.0 percent samples since the concentrations were determined by the mass-spectrograph. It is to be noted that all our Δh's are lower than those calculated. It is doubtful, however, if this is significant since we estimate that our experimental error is about 0.00040 in Δh. If we assume that our concentration of deuterium in the last sample is 76.5 percent then the difference between the Δh exp. and Δh calc. will be about 0.00084. This seems to be definitely larger than our experimental error.

While this experiment was conducted in the gaseous phase there is no reason to doubt that similar deviations from the classical value of the equilibrium constant will be found for reactions in condensed systems.

D. RITTENBERG
H. C. UREY

Department of Chemistry,
Columbia University,
New York, New York,
January 15, 1934.

[2] M. Bodenstein, Zeits. f. physik. Chemie **29**, 295 (1899).
[3] Bleakney, Phys. Rev. **34**, 157 (1929); **39**, 536 (1932).

Heavy Water Inert, Due to Low Association

Lewis and MacDonald[1] have reported the viscosities of heavy water over a considerable range of temperature. The very important question arises as to the effect of the extra proton in the nucleus of hydrogen upon the association of water. Bingham and Spooner[2] have given the temperature constants for ordinary hydrogen and for oxygen at 50, 100 and 200 rhes, as reproduced in Table I. As fluidities have been found to be additive, the temperature required to give ordinary water a fluidity of 200 rhes would be 131.6°K, provided that the water remained unassociated. As shown in Table I, the observed value (328.9°K) is very much higher, leading to an association of 2.50.

TABLE I.

	50 rhes	100 rhes	200 rhes
Hydrogen temperature constant (Bingham and Spooner)	45.9	50.4	59.3
Oxygen temperature constant	13.9	13.6	13.0
Observed temperature K for ordinary water	269.7	293.3	328.9
Calculated temperature K for ordinary water	105.7	114.4	131.6
Association of ordinary water	2.55	2.56	2.50
Deuterium temperature constant	91.8	100.8	118.6
Observed temperature K for deuterium oxide	277.8	301.7	(336.7)
Calculated temperature K for deuterium oxide	197.5	215.2	250.2
Association of deuterium oxide	1.41	1.40	(1.34)

The fluidity of heavy water is quite different from the fluidity of ordinary water, so that it is necessary to conclude that the additional proton affects the fluidity of water and presumably therefore the temperature constant of fluidity. (See Fig. 1.) If this is so, the simplest assumption is that the effect is additive, so that if the constant of hydrogen is 59.3 at 200 rhes the constant for deuterium is 118.6°, for the same fluidity. This would lead to a higher calculated temperature of 250.2° required to give deuterium oxide a fluidity of 200 rhes, again on the *proviso* that the water in question is non-associated. This is in accordance with the observed fact that heavy water is more viscous than

[1] Lewis and MacDonald, J. A. C. S. **55**, 4730 (1933).
[2] Bingham and Spooner, J. Rheology **3**, 221 (1932).

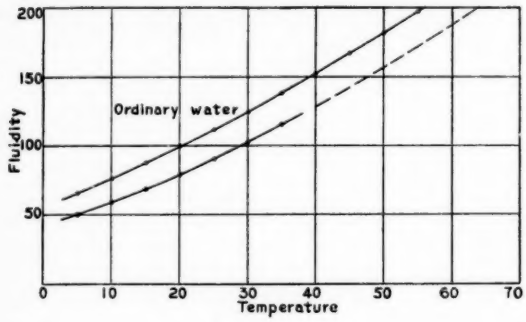


FIG. 1. Temperature-fluidity curve for deuterium oxide.

ordinary water. But even though heavy water is more viscous, the same method of calculation indicates that deuterium oxide is very much less associated than is ordinary water, 1.34 as compared with 2.50. If the oxygen of ordinary water possesses "residual valencies" as claimed by organic chemists, the additional protons in the deuterium would be expected to lower the free energy of the oxide. Deuterium oxide is not only less associated than ordinary water but the temperature coefficient of association of deuterium oxide is less, as proved by the association at 50 and 100 rhes. It has about the same association as such mildly associated substances as methyl formate or propionaldehyde. Deuterium oxide may therefore be regarded as rather inert chemically. The increased molecular weight would be expected to raise the freezing-point and boiling-point but the increase in the boiling-point given as 1.4° might be considerably greater were it not for the lower association. The decrease in surface tension, dielectric constant and refractive index are unanimous in indicating a lower association. The inert character of deuterium oxide is demonstrated by the fact that in it starch fails to react with enzyme, that seeds fail to germinate, that spirogyra fails to develop and that animal life perishes. It is assumed that deuterium oxide is not poisonous, since it is present in ordinary water, but it is quite clear that the life processes noted above may involve chemical reactions. Almost all aqueous solutions involve hydration. It is therefore not surprising that sodium chloride and barium chloride are relatively insoluble in heavy water, and it might be expected that the difference will prove to be less marked in the case of potassium chloride, silver nitrate and mercuric chloride, which dissolve with less evidence of hydration.

EUGENE C. BINGHAM
W. H. STEVENS, JR.

Lafayette College,
Easton, Pennsylvania,
January 15, 1934.